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Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NOx Burner. Volume 1. Technical Results

Acurex Corp., Mountain View, CA

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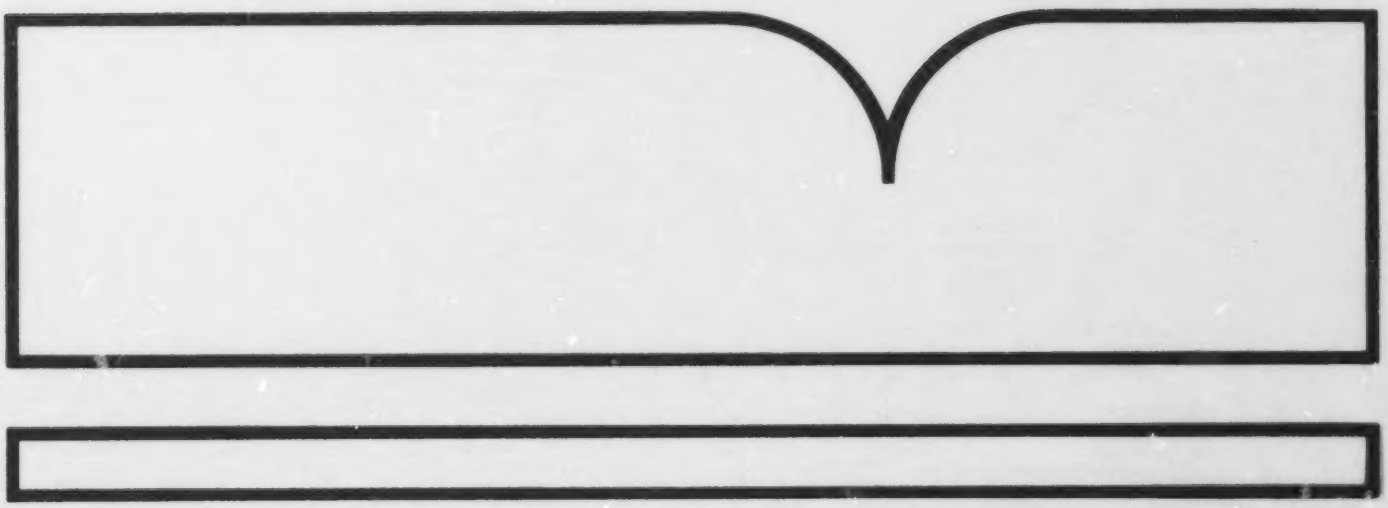

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ENVIRONMENTAL ASSESSMENT OF AN ENHANCED OIL RECOVERY STEAM GENERATOR EQUIPPED WITH A LOW-NO_x BURNER

Volume I
Technical Results

By

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16. ABSTRACT The report discusses results from sampling flue gas from an enhanced oil recovery steam generator (EOR steamer) equipped with an MHI PM low-NOx burner. The tests included burner performance/emission mapping tests, comparative testing of an identical steamer steamer equipped with a conventional burner, and comprehensive testing of the low-NOx-burner-equipped steamer. Comprehensive test measurements included continuous flue gas monitoring; source assessment sampling system testing with subsequent laboratory analysis to give total flue gas organics in two boiling point ranges and specific quantitation on the semivolatile organic priority pollutants; C1 to C6 hydrocarbon sampling; Methods 5/8 sampling for particulate and SO2 and SO3 emissions; and emitted particle size distribution tests using Andersen impactors. Full-load NOx emissions of 110 ppm (3% O2) could be maintained from the low-NOx burner at acceptable CO and smoke emissions, compared to about 300 ppm (3% O2) from the conventional-burner-equipped steamer. At this low-NOx condition, CO, SO2, and SO3 emissions were 93, 594, and 3.1 ppm, respectively. Particulate emissions were 39 mg/dscm with a mean particle diameter of 3 to 4 micrometers. Total organic emissions were 11.1 mg/dscm, almost exclusively volatile (C1 to C6) organics. Three PAHs were detected at from 0.1 to 1.4 micrograms/dscm.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Boilers	Stationary Sources	13A
Oil Burners	Low-NOx Burners	
Crude Oil	Environmental Assessment	11H, 08G
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SECTION 1

INTRODUCTION

This report describes and presents results for a set of environmental assessment tests performed for the Environmental Protection Agency's Air and Energy Engineering Research Laboratory (EPA/AEERL) under the Combustion Modification Environmental Assessment (CMEA) program, EPA Contract No. 68-02-3188. The CMEA started in 1976 with a 3-year study, the NO_x Control Technology Environmental Assessment (NO_x EA, EPA Contract No. 68-02-2160), having the following four objectives:

- Identify potential multimedia environmental effects of stationary combustion sources and combustion modification technology
- Develop and document control application guidelines to minimize these effects
- Identify stationary source and combustion modification R&D priorities
- Disseminate program results to intended users

During the first year of the NO_x EA, data for the environmental assessment were compiled and methodologies were developed. Furthermore, priorities for the schedule and level of effort to be devoted to evaluating the various source/fuel/control combinations were identified. This effort revealed major data gaps, particularly for noncriteria pollutants (organic emissions and trace elements) for virtually all combinations of stationary

combustion sources and combustion modification techniques. Consequently, a series of seven environmental field test programs was undertaken to fill these data gaps. The results of these tests are documented in seven individual reports (References 1-1 through 1-7) and in the NO_x EA final report summarizing the entire 3-year effort (Reference 1-8).

The current CMEA program has, as major objectives, the continuation of multimedia environmental field tests initiated in the original NO_x EA program. These new tests, using standardized Level 1 sampling and analytical procedures (Reference 1-9) are aimed at filling the remaining data gaps and addressing the following priority needs:

- Advanced NO_x controls
- Alternate fuels
- Secondary sources
- EPA program data needs
  - -- Residential oil combustion
  - -- Wood firing in residential, commercial, and industrial sources
  - -- High interest emissions determination (e.g., listed and candidate hazardous air pollutant species)
- Nonsteady-state operation

The petroleum reserves which can be recovered through primary production methods have been essentially exhausted in the oil fields in Kern County, California. These fields still contain significant reserves, although the remaining crude is too viscous to be produced by normal means. This crude is currently being produced using what has been termed enhanced oil recovery (EOR). In one popular process, near saturated (80 to 90 percent quality)

steam is injected into a field. This steam heats the oil, thereby decreasing its viscosity and allowing it to be pumped.

The steam for injection is raised by crude oil-fired steam generators (often termed steamers) which have uncontrolled NO_x emissions in the 300 ppm range. Since Kern County is only in borderline attainment of the NO_2 ambient air quality standard, EOR steamers have received close regulatory attention with respect to reducing NO_x emissions.

One approach to reducing NO_x emissions from these steamers incorporates a low-NO_x emission burner design. One such burner was developed in Japan by Mitsubishi Heavy Industries (MHI) and is currently marketed in the United States by CE-Natco (a steamer manufacturer).

A steamer equipped with an MHI low-NO_x burner was tested in the current CMEA program. These tests, described in this report, were conducted to quantify a broad emissions spectrum from the burner and to compare selected species emissions to those from a steamer equipped with a "standard" burner. Thus, a similar unit with a standard burner was also tested (in less depth, however) in this program.

In addition to the tests described in this report, another EOR steamer, this one equipped with a low-NO_x burner developed under EPA contract by the Energy & Environmental Research Corporation, was also tested. Results from these tests are documented in Reference 1-10.

Table 1-1 lists all the tests performed in the CMEA program, outlining the source tested, fuel used, combustion modifications implemented and the level of sampling and analysis performed in each case. Results of these test programs are discussed in separate reports.

TABLE 1-1. COMPLETED TESTS DURING THE CURRENT PROGRAM[a]

Source	Description	Test points unit operation	Sampling protocol	Test collaborator
Spark-ignited, natural-gas-fired reciprocating internal combustion engine	Large bore, 6-cylinder, opposed piston, 186-kW (250 Bhp)/cyl, 900-rpm Model 38TDS8-1/8	-- Baseline (pre-NSPS) -- Increased air-fuel ratio aimed at meeting proposed NSPS of 700 ppm corrected to 15 percent O_2 and standard atmospheric conditions	Engine exhaust: -- SASS -- Method 5 -- Gas sample (C_1-C_6 HC) -- Continuous NO, NO_x, CO, CO_2, O_2, CH_4, TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries
Compression ignition, diesel-fired, reciprocating internal combustion engine	Large bore, 6-cylinder opposed piston, 261-kW (350 Bhp)/cyl, 900-rpm Model 38TDD8-1/8	-- Baseline (pre-NSPS) -- Fuel injection retard aimed at meeting proposed NSPS of 600 ppm corrected to 15 percent O_2 and standard atmospheric conditions	Engine exhaust: -- SASS -- Method 8 -- Method 5 -- Gas sample (C_1-C_6 HC) -- Continuous NO, NO_x, CO, CO_2, O_2, CH_4, TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries
Low-NO_x, residential, condensing-heating system furnished by Karlsons Blueburner Systems Ltd. of Canada	Residential hot water heater equipped with M.A.N. low-NO_x burner, 0.55 ml/s (0.5 gal/hr) firing capacity, condensing flue gas	Low-NO_x burner design by M.A.N.	Furnace exhaust: -- SASS -- Method 8 -- Method 5 -- Gas sample (C_1-C_6 HC) -- Continuous NO, NO_x, CO, CO_2, O_2, CH_4, TUHC Fuel Waste water	New test
Rocketdyne/EPA low-NO_x residential forced warm air furnace	Residential warm air furnace with modified high-pressure burner and firebox, 0.83 ml/s (0.75 gal/hr) firing capacity	Low-NO_x burner design and integrated furnace system	Furnace exhaust: -- SASS -- Method 8 -- Controlled condensation -- Method 5 -- Gas sample (C_1-C_6 HC) -- Continuous NO, NO_x, CO, CO_2, O_2, CH_4, TUHC Fuel	New test

(continued)

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator
Pulverized coal-fired utility boiler, Conesville station	400-MW tangentially fired; new NSPS design aimed at meeting 301 ng/J NO_x limit	ESP inlet and outlet, one test	ESP inlet and outlet -- SASS -- Method 5 -- Controlled condensation -- Gas sample (C_1-C_6 HC) -- Continuous NO, NO_x, CO, CO_2, O_2 Coal Bottom ash ESP ash	Exxon Research and Engineering (ER&E) conducting corrosion tests
Nova Scotia Technical College industrial boiler	1.14 kg/s steam (9,000 lb/hr) firetube fired with a mixture of coal-oil-water (COW)	-- Baseline (COW) -- Controlled SO_2 emissions with limestone addition	Boiler outlet -- SASS -- Method 5 -- Method 8 -- Controlled condensation -- Gas sample (C_1-C_6 HC) -- Continuous O_2, CO_2, CO, NO_x Fuel	Envirocon performed particulate and sulfur emission tests
Adelphi University industrial boiler	1.89 kg/s steam (15,000 lb/hr) hot water firetube fired with a mixture of coal-oil-water (COW)	-- Baseline (COW) -- Controlled SO_2 emissions with soda ash (Na_2CO_3) addition	Boiler outlet -- SASS -- Method 5 -- Method 8 -- Controlled condensation -- Gas Sample (C_1-C_6 HC) -- Continuous O_2, CO_2, NO_x, SO_2, CO Fuel	Adelphi University
Pittsburgh Energy Technology Center (PETC) industrial boiler	3.03 kg/s steam (24,000 lb/hr) watertube fired with a mixture of coal-oil (COM)	-- Baseline test only with COM	Boiler outlet -- SASS -- Method 5 -- Controlled condensation -- Continuous O_2, CO_2, NO_x, TUHC, CO Fuel	PETC and General Electric (GE)

(continued)

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator
TOSCO Refinery vertical crude oil heater	2.54 Ml/day (16,000 bbl/day) natural draft process heater burning oil/refinery gas	-- Baseline -- Staged combustion using air injection lances	Heater outlet -- SASS -- Method 5 -- Controlled condensation -- Gas sample (C_1-C_6 HC) -- Continuous O_2, NO_x, CO, CO_2, HC -- N_2O grab sample Fuel oil Refinery gas	KVB coordinating the staged combustion operation and continuous emission monitoring
Mohave [illegible] industrial boiler	8.21 kg/s steam (65,000 lb/hr) watertube burning mixture of refinery gas and residual oil	-- Baseline -- Ammonia injection using the noncatalytic Thermal DeNO$_x$ Process	Economizer outlet -- SASS -- Method 5, 17 -- Controlled condensation -- Gas Sample (C_1-C_6 HC) -- Ammonia emissions -- N_2O grab sample -- Continuous O_2, NO_x, CO, CO_2 Fuels (refinery gas and residual oil)	New test
Industrial boiler	2.52 kg/s steam (20,000 lb/hr) watertube burning wood waste	-- Baseline (dry wood) -- Wet (green) wood	Boiler outlet -- SASS -- Method 5 -- Controlled condensation -- Gas sample (C_1-C_6 HC) -- Continuous O_2, NO_x, CO Fuel Flyash	North Carolina Department of Natural Resources, EPA IERL-RTP
Industrial boiler	3.16 kg/s steam (29,000 lb/hr) firetube with refractory firebox burning wood waste	-- Baseline (dry wood)	Outlet of cyclone particulate collector -- SASS -- Method 5 -- Controlled condensation -- Gas sample (C_1-C_6 HC) -- Continuous O_2, NO_x, CO Fuel Bottom ash	North Carolina Department of Natural Resources, EPA IERL-RTP

(continued)

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test callaborator
Enhanced oil recovery steam generator	15 MW (50 million Btu/hr) steam generator burning crude oil equipped with MHI low-NO_x burner	-- Performance mapping -- Low NO_x operation	Steamer outlet: -- SASS -- Method 5 -- Method 8 -- Andersen impactors -- Gas sample (C_1 - C_6 HC) -- Continuous O_2, NO_x, CO, CO_2 -- N_2O grab sample Fuel	Getty Oil Company, CE-Natco
Pittsburgh Energy Technology Center (PETC) industrial boiler	3.03 kg/s steam (24,000 lb/hr) watertube fired with a coal-water slurry (CWS)	-- Baseline test only with CWS	Boiler outlet: -- SASS -- Method 5 -- Method 8 -- Gas sample (C_1 - C_6 HC) -- Continuous O_2, NO_x, CO, CO_2, TUHC -- N_2O grab sample Fuel Bottom ash Collector hopper ash	PETC and General Electric
Spark-ignited, natural gas-fuel reciprocating internal combustion engine -- nonselective NO_x reduction catalyst	610 kW (818 hp) Waukesha rich-burn engine equipped with DuPont NSCR system	-- Low NO_x (with catalyst) -- 15-day emissions monitoring	Catalyst inlet and outlet -- SASS -- NH_3 -- HCN -- N_2O grab sample -- Continuous O_2, CO_2, NO_x TUHC Lube oil	Southern California Gas Company
Industrial boiler	180 kg/hr steam (400 lb/hr) stoker fired with a mixture of coal and waste plastic beverage containers	-- Baseline (coal) -- Coal and plastic waste	Boiler outlet -- SASS -- VOST -- Method 5 -- Method 8 -- HCl -- Continuous O_2, NO_x, CO, CO_2, TUHC -- N_2O grab sample Fuel Bottom ash Cyclone ash	Vermont Agency of Environmental Conservation

(continued)

TABLE 1-1. (concluded)

Source	Description	Test points unit operation	Sampling protocol	Test callaborator
Industrial boiler	7.6 kg/s steam (60,000 lb/hr) watertube retrofit for coal-water-slurry (CWS) firing	-- Baseline test with CWS -- 30-day emissions monitoring	Boiler outlet -- SASS -- VOST -- Method 5 -- Method 8 -- Gas sample (C_1-C_6 HC) -- N_2O grab sample -- Continuous NO_x, CO, CO_2, O_2, TUHC, SO_2 Fuel	EPRI, DuPont
Enhanced oil recovery steam generator	15 MW (50 million Btu/hr) steam generator burning crude oil, equipped with the EPA/EER low NO_x burner	-- Low NO_x (with burner) -- 30-day emission monitoring	Steamer outlet -- SASS -- VOST -- Method 5 -- Method 8 -- Controlled condensation -- Andersen impactors -- Grab sample (C_1-C_6 HC) -- N_2O grab sample -- Continuous NO_x, CO, CO_2, O_2, SO_2 Fuel	Chevron U.S.A., EERC
Spark-ignited, natural gas-fired reciprocating internal combustion engine -- selective NO_x reduction catalyst	1490 kW (2000 hp) Ingersoll-Rand lean burn engine equipped with Englehard SCR system	-- Low NO_x (with catalyst) -- 15-day emissions monitoring	Catalyst inlet and outlet -- SASS -- VOST -- NH_3 -- HCN -- N_2O grab sample -- Continuous O_2, CO_2, CO, NO, NO_x, NO_x + NH_3 Lube oil	Southern California Gas Company

[a]Acronymns used in the table: EERC, The Energy and Environmental Research Corporation; EPA IERL-RTP, The Environmental Protection Agency's Industrial Environmental Research Laboratory-Research Triangle Park; EPRI, The Electric Power Research Institute; HC, hydrocarbons; NSCR, nonselective catalytic reduction; NSPS, new source performance standard; SASS, source assessment sampling system; SCR, selective catalytic reduction; TUHC, total unburned hydrocarbon; VOST, volatile organic sampling train

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SECTION 2

SOURCE DESCRIPTION

Tests were performed on two CE-Natco model STOF steam generators rated at 50 million Btu/hr heat output. One unit was equipped with a standard North American burner; the other had been retrofitted with the PM low-NO_x burner manufactured by Mitsubishi Heavy Industries (MHI). The primary objective of the tests was to measure the NO_x reduction performance of this burner as a function of its operational parameter settings (when compared to a standard burner) and to obtain data on emissions of noncriteria pollutant categories and species at a nominal low-NO_x setting.

Figure 2-1 illustrates the physical design of the MHI PM burner. As shown, the rectangular burner throat is divided into five nozzles. Typically about 30 percent of the total combustion air is delivered through the central primary air nozzle. This air is mixed with a centralized oil spray comprising approximately half the total fuel fired, forming an oxygen deficient diffusion flame. A premixed flame is obtained by mixing the remaining fuel with about 60 percent of the total air, evenly delivered through each of the upper and lower nozzles. This mixing takes place in a zone offset from the burner which delays ignition until the fuel and air have mixed.

The remaining combustion air (about 10 percent) is delivered through an overfire air (OFA) injection system which injects this air approximately

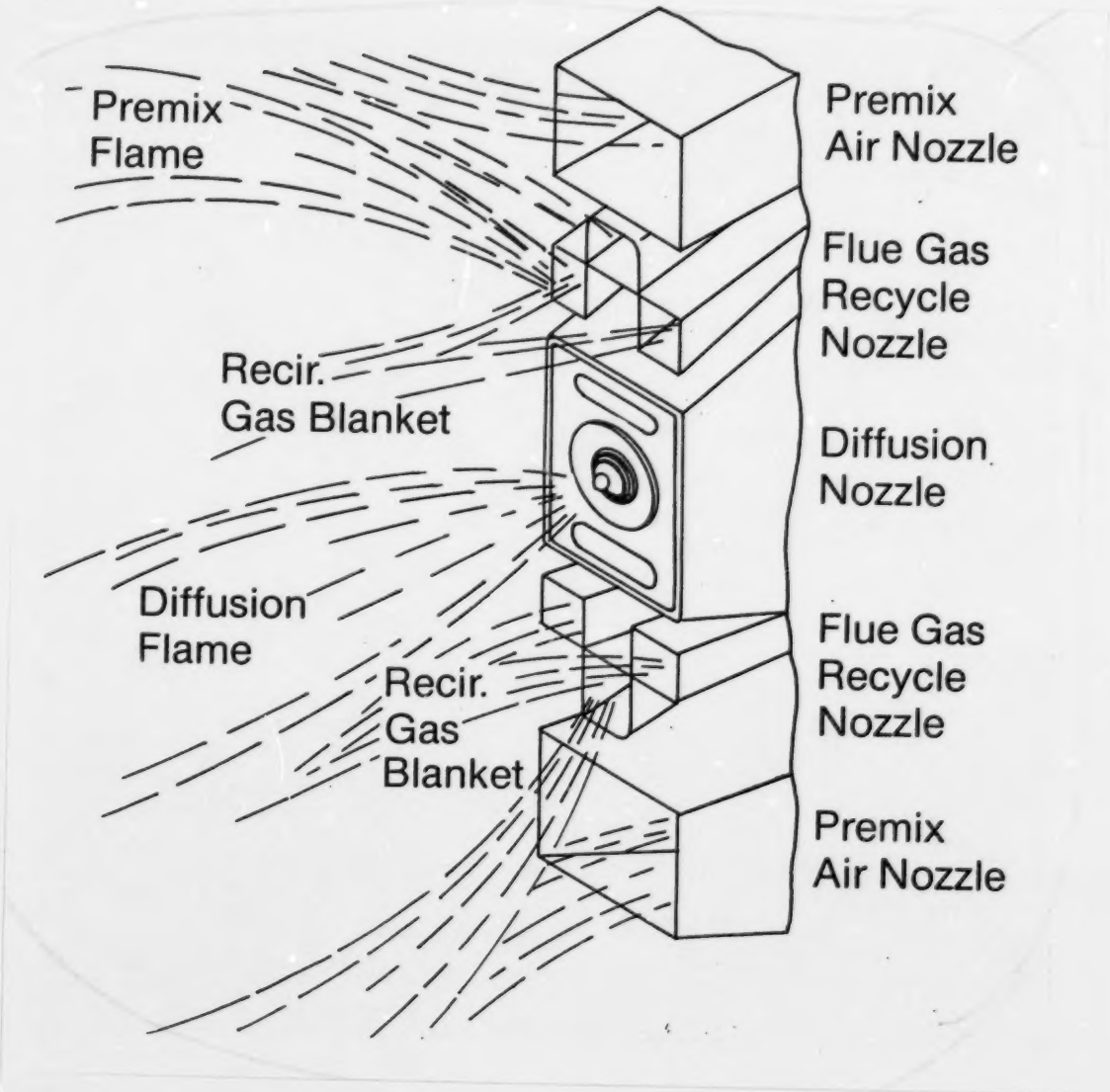


Figure 2-1. The MHI PM burner nozzle.

halfway down the length of the cylindrical furnace through three sets of three ports equally spaced around the furnace circumference. This OFA is designed to ensure that sufficient excess air and mixing are achieved before combustion gas leaves the furnace.

Recirculated flue gas is delivered to the nozzles separating the central (diffusion) and outer (premix) air nozzles. This gas is used to shape the diffusion flame and to maintain separation between the diffusion and premixed flames. Typically about 15 percent of the total combustion product gas is recirculated.

Figure 2-2 shows a sketch of the steamer retrofitted with the burner system. The additional flue gas recirculation (FGR) and OFA systems along with the burner are shown.

In the test program performed, one day of flue gas emission testing was performed on the steamer equipped with the conventional burner. In these tests, flue gas NO_x emissions were measured at two steamer loads while varying the excess air fuel. The steamer equipped with the low-NO_x burner was then subjected to two days of performance/emissions mapping tests in which flue gas composition (NO_x, CO, CO_2, O_2 and smoke) was characterized while varying burner operation at full steamer load. In these tests, the following were varied: the FGR rate; the relative distribution of combustion air among the premixed flame nozzles, the diffusion flame nozzles, and the OFA ports; and the overall excess air level. Finally, comprehensive emissions testing (flue gas organics, particulate load, particle-size distribution, and SO_2 and SO_3 emissions) was performed on the low-NO_x burner-equipped steamer with the burner set at a nominal low-NO_x condition.

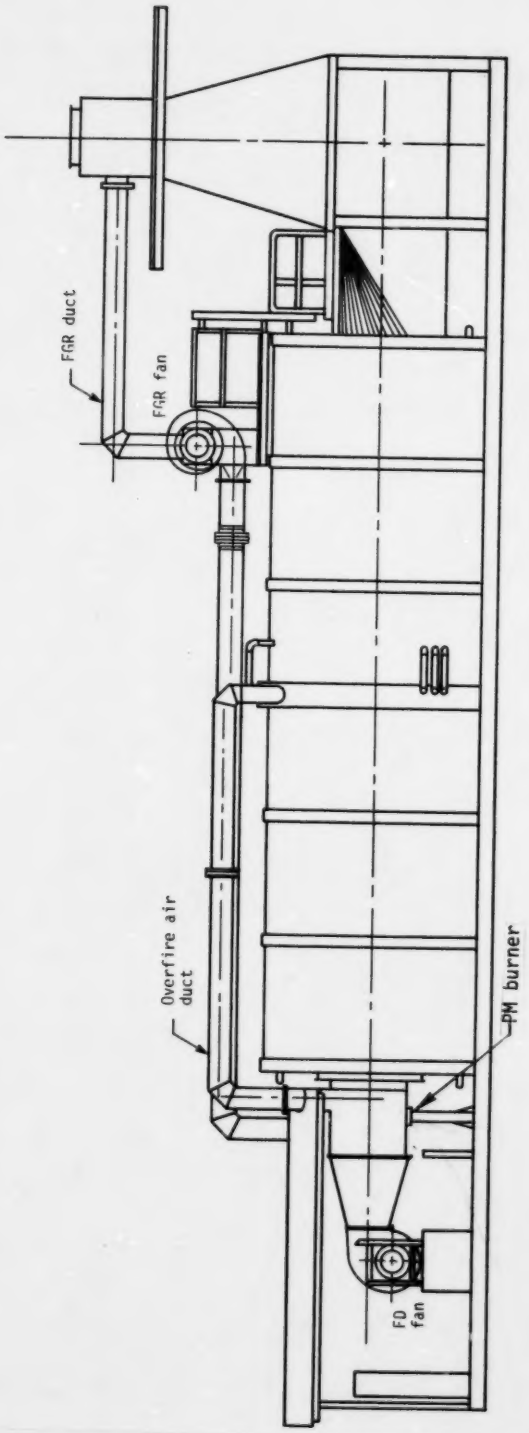


Figure 2-2. Schematic of test steamer.

The fuel fired in both steamers for all tests was local Kern County crude. The fuel ultimate analysis is given in Table 2-1.

The concentrations of 72 trace elements in the fuel were also obtained using spark source mass spectrometry (SSMS) supplemented by atomic absorption spectrometry. Results of these analyses are given in Table 2-2.

TABLE 2-1. FUEL ULTIMATE ANALYSIS

Component (wt percent)	
Carbon	86.88
Hydrogen	10.84
Sulfur	1.06
Nitrogen	0.76
Oxygen	0.43
Ash	0.03
Higher heating, MJ/kg value (Btu/lb)	43.2 (18,560)
API gravity	13.3

TABLE 2-2. FUEL TRACE ELEMENT CONCENTRATIONS

Element	Concentration (µg/g)	Element	Concentration (µg/g)	Element	Concentration (µg/g)
Aluminum	4.0	Holmium	--	Samarium	--
Antimony	0.07	Iodine	--	Scandium	0.08
Arsenic	0.4	Iridium	--	Selenium	0.2
Barium	0.5	Iron	95	Silicon	34
Beryllium	<0.01	Lanthanum	0.4	Silver	0.03
Bismuth	--[a]	Lead	0.3	Sodium	22
Boron	0.2	Lithium	0.1	Strontium	0.5
Bromine	0.3	Lutetium	--	Tantalum	2
Cadmium	--	Magnesium	14	Tellurium	0.06
Calcium	48	Manganese	0.4	Terbium	--
Cerium	0.2	Mercury	<0.01	Thallium	--
Cesium	--	Molybdenum	1	Thorium	0.8
Chlorine	4	Neodymium	<0.2	Thulium	--
Chromium	0.8	Nickel	90	Tin	0.07
Cobalt	2	Niobium	<0.03	Titanium	3
Copper	5	Osmium	--	Tungsten	--
Dysprosium	--	Palladium	--	Uranium	--
Erbium	--	Phosphorus	0.8	Vanadium	80
Europium	--	Platinum	--	Ytterbium	--
Fluorine	27	Potassium	4	Yttrium	0.6
Gadolinium	--	Praseodymium	0.06	Zinc	1
Gallium	0.5	Rhenium	--	Zirconium	0.3
Germanium	0.2	Rhodium	--		
Gold	--	Rubidium	0.02		
Hafnium	--	Ruthenium	--		

[a] -- denotes present at less than the detection limit of 0.02 µg/g.

SECTION 3

EMISSION RESULTS

As noted in Section 2, the objectives of these tests were to evaluate the NO_x emission reduction performance of the MHI PM low NO_x burner system retrofitted to an enhanced oil recovery steam generator and to quantitate emissions of noncriteria pollutant species from the retrofit steamer. To satisfy these objectives a brief series of flue gas emission measurement tests was performed on an identical unit equipped with a conventional burner. A relatively comprehensive series of performance/emission mapping tests was performed next on the unit equipped with the low NO_x burner. Finally, a set of comprehensive environmental assessment flue gas characterization tests was performed on the low NO_x burner equipped-steamer with burner operation set at a nominal low NO_x setting.

Section 3.1 summarizes results of the tests of the conventional burner-equipped steamer and the performance/emission mapping tests on the low NO_x burner-equipped steamer. Results of the comprehensive emission testing of the low NO_x burner-equipped steamer are discussed in Section 3.2.

3.1 PERFORMANCE/EMISSION MAPPING TESTS

Flue gas emissions of NO_x, CO, CO_2, O_2, and stack gas smoke readings were measured on the steamer equipped with a conventional North American burner at two loads (full load and about 75 percent of rated capacity) and several excess air settings. These measurements were performed at the stack

using a continuous flue gas monitoring system as described in Appendix A. To supplement these measurements, Getty Oil Company personnel performed complementary monitoring of the combustion gas at the steamer furnace exit.

Results of these tests are summarized in Table 3-1. The data in the table clearly suggest that there was some combustion gas dilution through air inleakage between the furnace outlet sampling location and the stack sampling location. Stack O_2 levels are consistently higher and CO_2 consistently lower than corresponding furnace outlet levels. CO levels (corrected to 3 percent O_2) are comparable at the two locations at full load. However, NO_x levels at full load were generally about 40 to 50 ppm higher at the stack location than at the furnace outlet. At 75 percent load, NO_x levels at both locations were comparable; however, CO levels were apparently increased. Reasons for both these apparent increases (if they were indeed real) can only be speculated.

The stack location NO_x emissions data are plotted in Figure 3-1 as NO_x versus stack gas O_2. The figure shows a steady decrease in NO_x emissions as excess air is reduced until flue gas O_2 falls below about 3 percent. Below this O_2 level, the rate of NO_x emissions increases. However, referring to Table 3-1, as flue gas O_2 is decreased below 3 percent, the smoke number increases to unacceptable levels. For practical operation, then, the conventional burner appears capable of attaining full load NO_x emissions of about 300 ppm (3 percent O_2) with flue gas O_2 about 3.7 percent at acceptable CO emissions and smoke number. At 75 percent load, NO_x emissions are reduced to about 250 ppm (3 percent O_2) at flue gas O_2 of 4.0 percent and acceptable CO and smoke number.

Following the conventional burner-equipped unit testing, a relatively comprehensive series of performance emission mapping tests was performed on

TABLE 3-1. FLUE GAS EMISSIONS SUMMARY: CONVENTIONAL BURNER

Test no.	Fuel flow (l/s)	Fuel flow (BPD)	Heat input (MW)	Heat input (million Btu/hr)	Stack[a] O_2 (%)	Stack[a] CO_2 (%)	Stack[a] CO (ppm)[c]	Stack[a] NO_x (ppm)[c]	Stack[a] Smoke	Furnace outlet[b] O_2 (%)	Furnace outlet[b] CO_2 (%)	Furnace outlet[b] CO (ppm)[c]	Furnace outlet[b] NO_x (ppm)[c]	Furnace outlet[b] SO_2 (ppm)[c]
Full load														
1	0.39	210	16.3	55.5	3.7	12.8	23	302	--	3.0	14.1	42	263	580
2	0.39	210	16.3	55.5	5.1	12.0	34	340	3.0	4.4	12.9	48	288	580
3	0.39	210	16.3	55.5	6.6	10.8	31	365	4.0	6.2	11.5	49	305	584
4	0.39	210	16.3	55.5	3.7	13.1	42	305	4.0	2.8	14.1	42	256	593
5	0.39	210	16.3	55.5	2.9	12.2	54	278	8.0	1.9	14.8	46	227	598
6	0.39	210	16.5	56.3	2.3	14.4	46	197	8.5	1.3	15.3	54	206	603
75% load														
7	0.29	160	12.4	42.3	4.2	13.3	78	246	4.0	2.8	14.1	40	254	584
8	0.29	160	12.4	42.3	6.4	11.7	96	296	2.5	5.3	12.1	46	300	608
9	0.29	160	12.4	42.3	6.1	12.7	133	290	3.0	4.0	13.2	42	277	578

[a]Emission measurements by Acurex.
[b]Emission measurements by Getty Oil Company.
[c]Dry at 3 percent O_2.

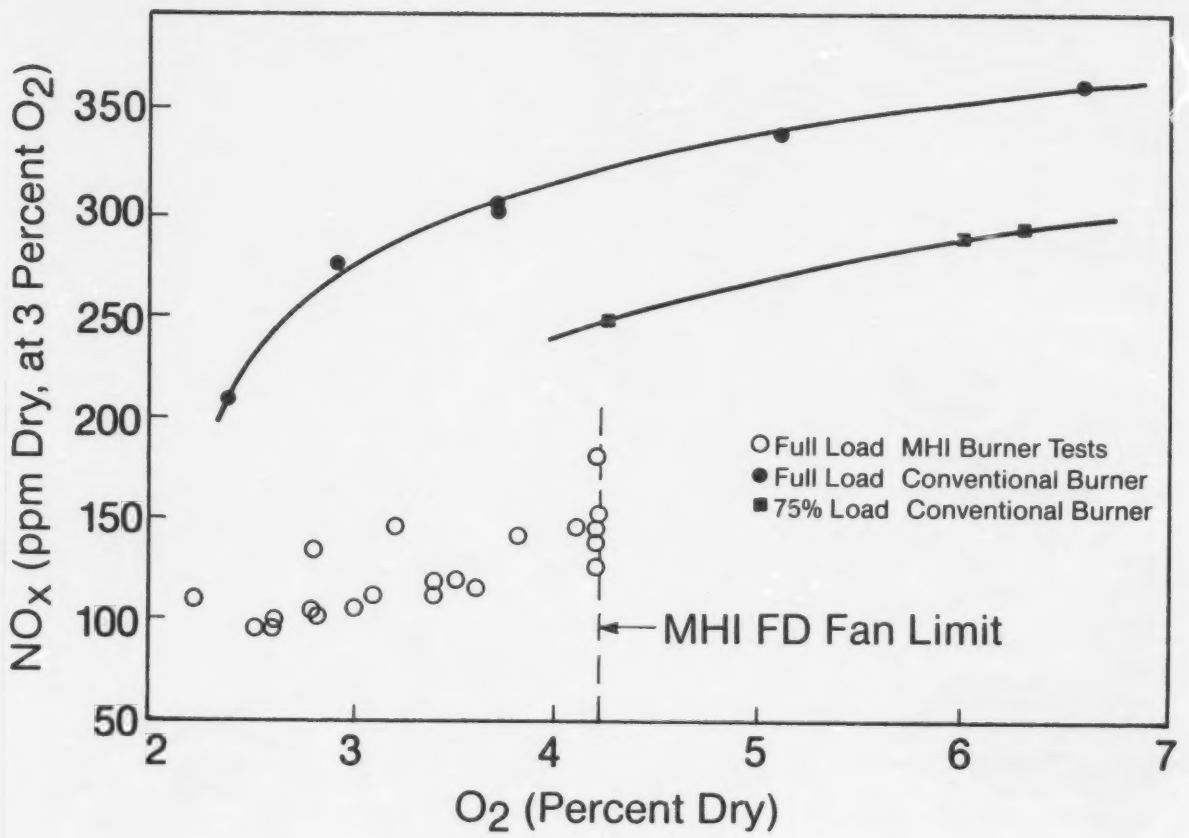


Figure 3-1. NO_x emissions versus flue gas O_2.

the steamer equipped with the low NO_x burner. Recall from Section 2 that this burner directs combustion air to a central diffusion flame nozzle, outboard premixed flame nozzles, and overfire air injection ports. Thus, the distribution of combustion air among these streams, as well as the total air fired, are adjustable burner operating parameters. In addition, the rate at which flue gas is recirculated to the burner (to separate the diffusion and premixed air flames) is a further adjustable parameter. All of these were varied in the testing performed.

Results of the performance/emission mapping tests are summarized in Table 3-2. Again, flue gas composition both at the steamer stack and at the furnace outlet (measurements performed by Getty Oil Company personnel) are shown. For these tests there was general agreement between the stack O_2 and CO_2 readings and those at the furnace outlet. This suggests that negligible air inleakage occurred between these locations for the low NO_x burner-equipped steamer, in contrast to the apparent case for the steamer with the conventional burner. Corresponding NO_x and CO levels were, in general, similarly comparable (although for a few test points stack CO levels were significantly higher than furnace outlet levels).

The data in Table 3-2 show that NO_x emissions from the unit varied from 95 to 180 ppm (corrected to 3 percent O_2) with changes in the parameters investigated. Certain conditions resulted in NO_x emissions at the stack below 100 ppm (3 percent O_2, dry), but these were, in general, accompanied by high CO emissions and high smoke spot. Conditions which resulted in NO_x in the 110 ppm range with moderate CO are also noted.

The variation in NO_x emissions with overall excess air (stack gas O_2) for this unit was shown in Figure 3-1. The scatter in the figure results

TABLE 3-2. MHI BURNER PERFORMANCE TEST RESULTS

			Air distribution		Fuel rate		Heat input		Stack[b]						Furnace outlet[c]					
Test no.	FGR rate (%)	OFA (%)	Premix[a] flame air (%)	Diffusion[a] flame air (%)	(l/s)	(BPD)	(MW)	(Million Btu/hr)	O_2 (%)	CO_2 (%)	CO (ppm)[d]	NO_x (ppm)[d]	TUHC (ppm)[d]	Smoke	O_2 (%)	CO (ppm)[d]	CO_2 (%)	NO_x (ppm)[d]	SO_2 (ppm)[d]	
1	8.9	19	48	33	0.383	208	16.1	55.0	3.5	13.4	99	119	3.2	>10	4.3	70	12.9	124	597	
2	9.4	18	52	30	0.385	209	16.2	55.2	2.7	13.9	266	102	4.4	10	3.3	80	13.9	113	594	
3	13.4	19	52	29	0.381	207	16.0	54.7	2.6	13.9	215	99	3.2	9.5	3.1	80	13.9	108	582	
4	9.9	19	53	29	0.390	212	16.4	56.0	2.5	14.0	236	95	5.3	10	3.1	73	14.0	109	592	
5	9.9	13	52	35	0.379	206	16.0	54.5	2.6	14.0	269	97	3.9	8	3.0	76	13.9	105	576	
6	9.4	15	51	34	0.377	205	15.9	54.2	3.4	13.9	60	119	2.2	6	4.0	59	13.0	126	573	
7	8.8	15	51	34	0.388	211	16.3	55.8	3.8	13.3	60	140	1.4	3.5	4.4	44	12.9	140	581	
8	9.1	11	56	33	0.386	210	16.3	55.5	3.2	13.2	51	145	1.1	3.5	3.3	45	13.9	144	568	
9	9.8	9	57	34	0.386	210	16.3	55.5	2.2	14.6	79	110	1.0	8	2.3	58	14.5	112	585	
10	9.3	8	57	35	0.388	211	16.3	55.8	3.1	13.3	141	111	4.5	10	2.2	104	14.7	102	616	
11	8.8	8	57	35	0.386	210	16.3	55.5	4.1	12.5	70	145	8.5	6	3.2	54	13.8	126	595	
12	8.2	8	58	34	0.396	215	16.7	56.8	4.2	12.5	64	180	8.6	3.5	4.2	46	12.9	174	570	
13	8.4	8	55	37	0.388	211	16.3	55.8	4.2	12.4	51	126	1.8	4	4.6	55	12.5	125	587	
14	8.8	8	55	37	0.390	212	16.4	56.0	3.4	13.0	85	111	1.1	8	3.6	67	13.5	114	573	
15	6.6	8	55	37	0.390	212	16.4	56.0	4.2	12.3	66	131	1.4	6	4.5	58	12.7	131	572	
16	2.6	8	55	37	0.390	212	16.4	56.0	4.2	12.3	54	152	1.1	2.5	4.6	53	12.6	149	582	
17	8.4	7	59	34	0.405	220	17.0	58.2	4.2	12.6	60	143	1.4	4	4.1	50	13.1	144	556	
18	9.1	6	58	36	0.377	205	15.9	54.2	3.6	12.9	62	116	0.5	6	3.3	64	13.8	113	558	
19	9.8	7	58	35	0.386	210	16.3	55.5	2.8	13.5	80	106	0	8	2.3	87	14.5	98	574	
20	9.8	3	62	35	0.388	211	16.3	55.8	2.8	13.6	64	133	0	6	2.5	55	14.5	126	583	
21 (SASS)	9.5	10	54	36	0.386	210	16.3	55.5	3.0	13.3	93	106	0	8	2.5	68	14.5	108	586	

[a]Premix and diffusion nozzle combustion air flows were not measured. Values shown here were estimated based on blower discharge pressure and static pressure readings in the windbox for diffusion and premix zones.
[b]Emission measurements by Acurex.
[c]Emission measurements by Getty Oil Company.
[d]Dry at 3 percent O_2.

from changes in NO_x emissions with the split in air flowrates among the diffusion and premixed flames and the OFA ports, and FGR rates at constant overall excess air. In general, though, NO_x emissions with the low-NO_x burner at full load were roughly half those of the conventional burner at a given flue gas O_2.

Figure 3-2 shows steamer stack gas CO emissions versus stack gas O_2 for both burners at full load. Again the scatter in the data for the low-NO_x burner results from variations in air distribution and FGR rate at constant stack O_2. The data in Figure 3-2 show that CO emissions from the low-NO_x burner increased steeply at flue gas O_2 below 2.5 to 3.0 percent. This contrasts with conventional burner behavior where CO emissions were still low at flue gas O_2 down to 2.5 percent. The higher CO levels from the low-NO_x burner, which were accompanied by high smoke spot (see Table 3-2) are attributed to flame impingement which was observed at the 4 and 8 o'clock positions at virtually all burner settings. Higher CO levels are attributed to increased flame impingement and excessively low diffusion zone stochiometries during low O_2 and high OFA tests.

The effect of OFA flowrate on both CO and NO_x levels for the low-NO_x burner is illustrated in Figure 3-3. CO levels decrease sharply at OFA rates below 10 percent. At 3 percent OFA, CO levels are nearly those of the conventional burner (see Figure 3-2). NO_x emissions at minimum OFA, however, are not significantly higher than those at high OFA rates.

The effect of FGR on NO_x and CO emissions from the low-NO_x burner is shown in Figure 3-4. FGR had a greater effect at a higher O_2 and lower OFA levels (4 percent and 8 percent OFA) than it did at lower O_2 and higher OFA levels (O_2 of 2.6 percent and 19 percent OFA). CO responded in an opposite

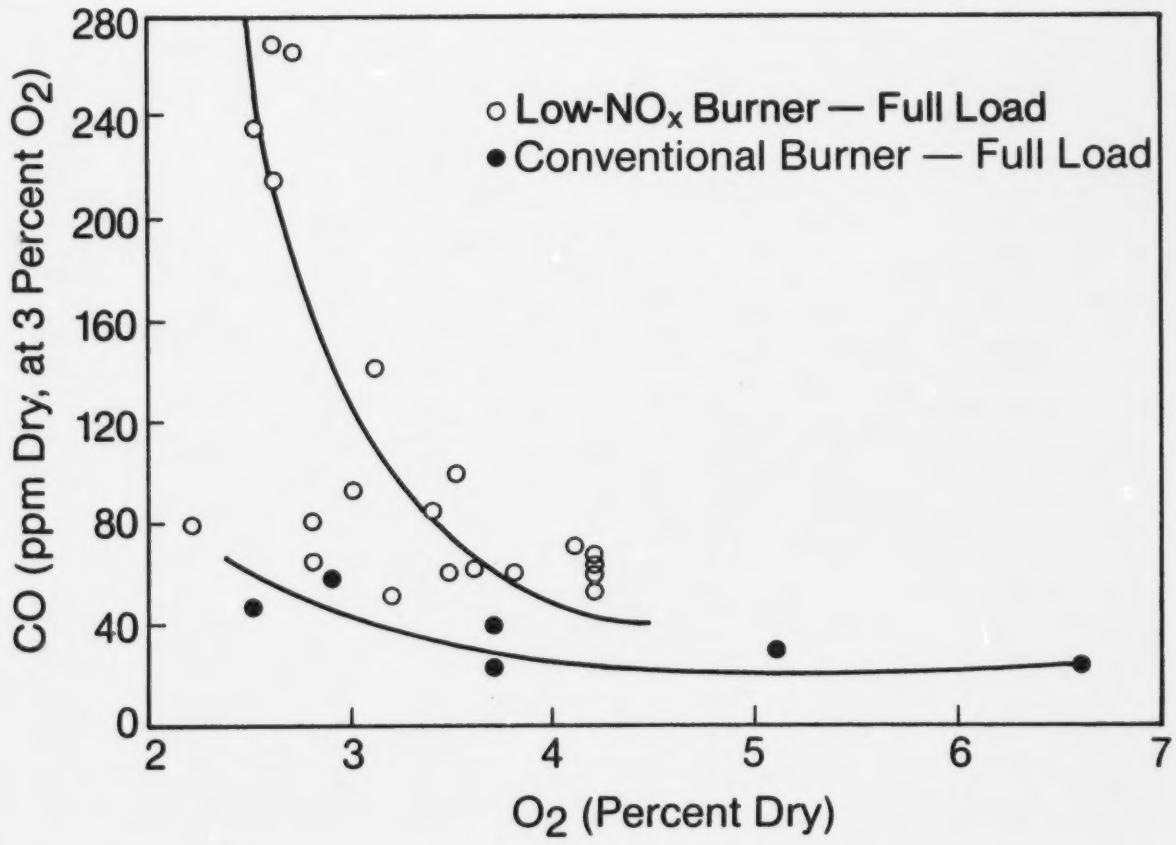
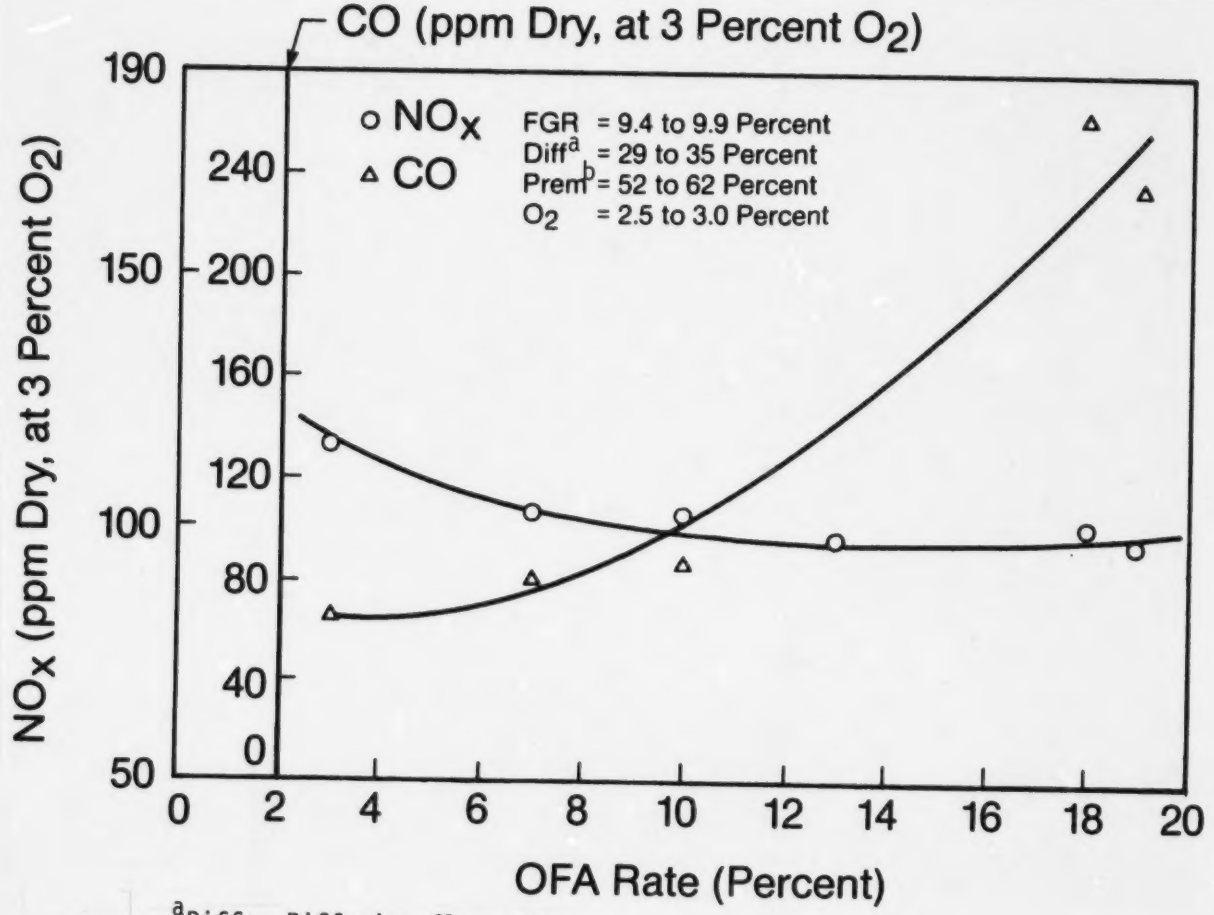
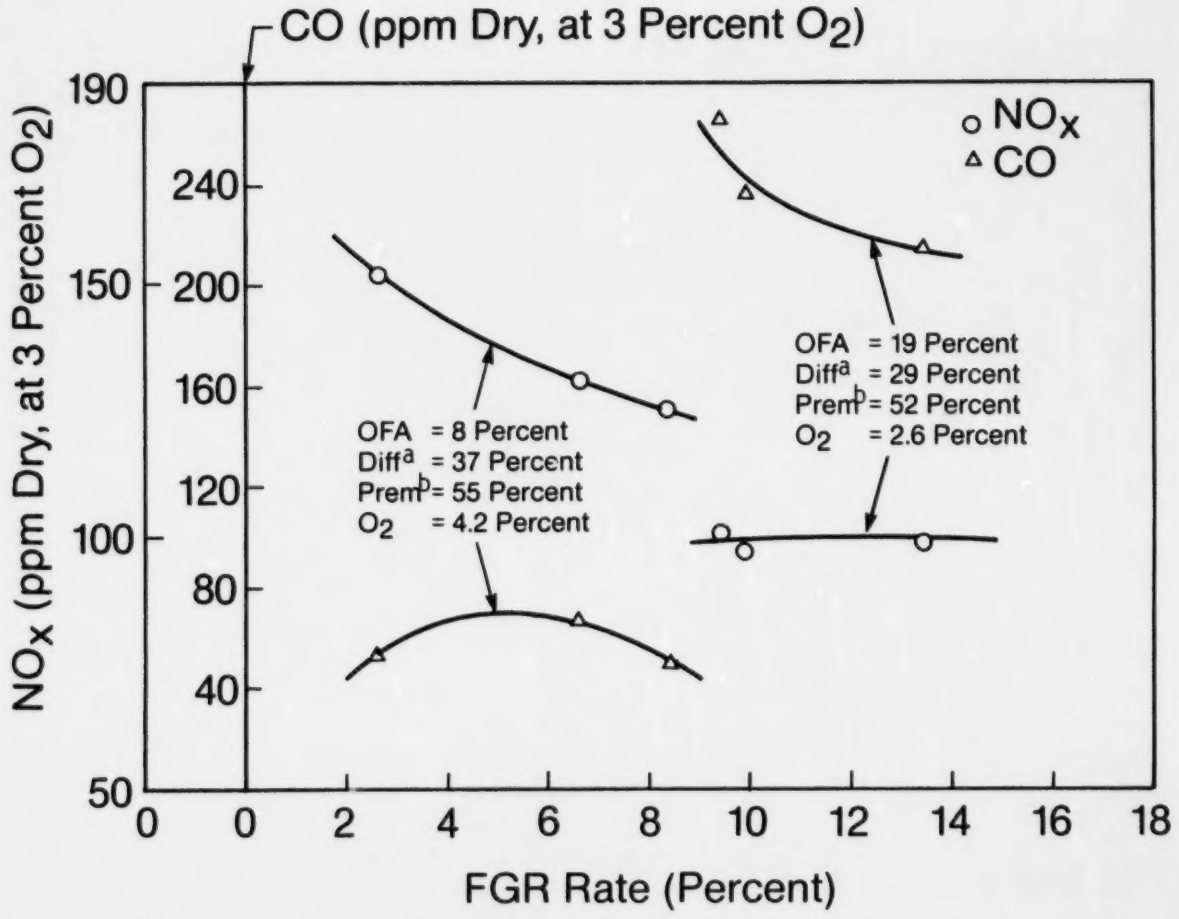


Figure 3-2. CO emissions versus flue gas O_2.



[a]Diff: Diffusion flame air
[b]Prem: Premixed flame air

Figure 3-3. Effect of OFA rate on NO_X and CO emissions from the low-NO_X burner.



[a]Diff: Diffusion flame air
[b]Prem: Premixed flame air

Figure 3-4. Effect of FGR rate on NO_x and CO emissions from the low NO_x burner.

manner. This can be explained in part by the greater mixing occurring at higher burner stoichiometries combined with lower FGR rates. This mixing tended to partly cancel the low-NO_x properties of the split flame. Conversely, the higher FGR rates combined with lower burner stoichiometry, while keeping the flames separate, will tend to cause greater impingement of the premix flame, which increased the CO levels.

Figure 3-5 shows a crossplot of the NO_x/CO emission data for the low-NO_x burner. This figure shows that, as the burner is adjusted to give NO_x emissions below about 110 ppm (3 percent O_2), CO emissions (and smoke, see Table 3-2) increase significantly. Thus, for this burner/steamer combination, minimum NO_x emissions at acceptable operation appear to be 110 ppm.

3.2 ENVIRONMENTAL ASSESSMENT TESTING

Following the performance/emission mapping tests discussed in Section 3.2, a set of burner operating conditions was selected for comprehensive emissions testing. The sampling protocol for these comprehensive tests included:

- Continuous monitoring for NO_x, O_2, CO, CO_2, and total unburned hydrocarbons (TUHC)
- Source assessment sampling system (SASS) for particulate size fractionation, and organic emissions
- EPA Method 5/8 for particulate mass emissions, and SO_2 and SO_3 emissions
- Andersen impactor train sampling for particle size distribution determination

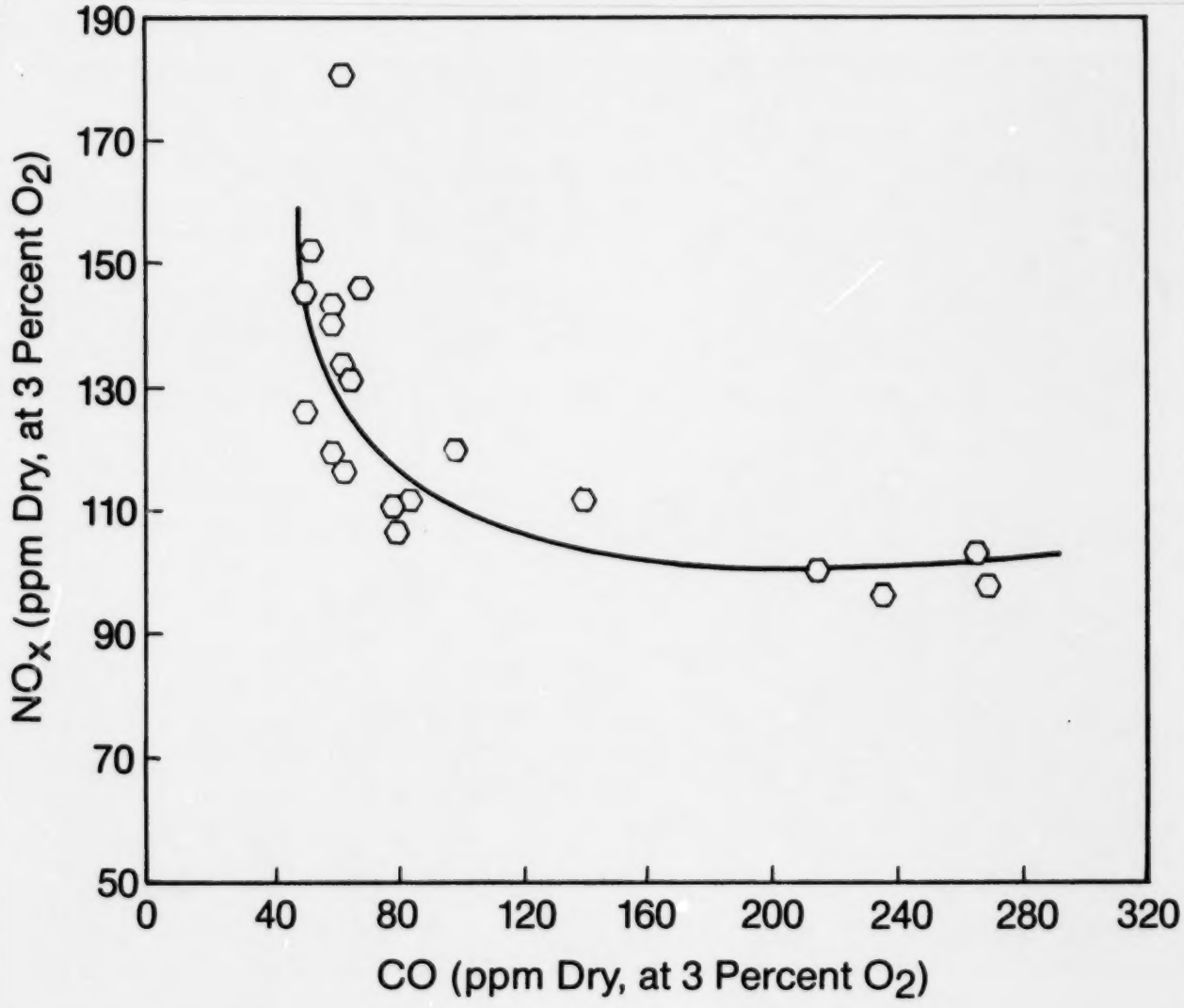


Figure 3-5. NO_x emissions versus CO for the MHI low NO_x burner.

- Grab sample for onsite analysis of C_1 to C_6 hydrocarbons by gas chromatography (GC)
- Grab sample for laboratory analysis of N_2O

All flue gas sampling for these tests was performed at the steamer stack. In addition, as for other testing performed in this program, Getty Oil Company personnel performed continuous flue gas monitoring at the steamer furnace outlet.

The analysis protocol for SASS samples included:

- Analyzing SASS train samples for total organic content in two boiling point ranges: 100° to 300°C by total chromatographable organics (TCO) analysis and greater than 300°C by gravimetry (GRAV)
- Analyzing the SASS train sorbent module and particulate extracts for the 58 semivolatile organic priority pollutant species including many of the PAH compounds
- Performing infrared (IR) spectrometry analysis of the GRAV residue of organic sample extracts
- Performing direct insertion probe low resolution mass spectrometry (LRMS) analysis of selected sample extracts

All aspects of the sampling and analysis protocols conformed to a modified EPA Level 1 protocol (Reference 3-1). Details of the procedures used are discussed in Appendix A.

Bioassay testing of SASS samples, a normal part of the comprehensive testing performed in this project, was not done in these tests due to the limited amount of particulate sample obtained and the very low organic content of the sorbent module extract.

Results of these comprehensive tests are discussed in the following subsections. Section 3.2.1 further details the steamer operating condition during the tests performed; Section 3.2.2 presents the criteria pollutant and other gas phase species emission results; and Section 3.3.3 summarizes organic category and species emission results.

3.2.1 Burner and Steamer Operation

The burner operating conditions selected for comprehensive testing matched those noted for Test 21 in Table 3-2. This operating point was selected since it represented about a minimum NO_x condition with CO emissions below 100 ppm (see Figure 3-5). The specific steamer and burner operating conditions for these tests are summarized in Table 3-3.

The steamer efficiency noted in Table 3-3 was calculated based on the ASME heat loss method (ASME PTC 4.1). The relative contributions to the calculations are summarized in Table 3-4. As shown in this table, most of the efficiency loss was through dry gas loss and moisture loss from the fuel hydrogen. The overall efficiency noted (82.8 percent) compares favorably to the efficiency of conventional burner-equipped units.

3.2.2 Criteria Pollutant and Other Gas Phase Species Emissions

Table 3-5 summarizes the gaseous and particulate emission levels measured during the comprehensive tests. Continuous emission monitor measurements from both the stack location and the furnace outlet location (obtained by Getty Oil personnel) are noted in the table. As shown in the table, steamer stack NO_x emissions were just below 110 ppm (3 percent O_2) with CO emissions of 93 ppm (3 percent O_2), negligible TUHC emissions, and a smoke reading of 8.

TABLE 3-3. STEAMER/BURNER OPERATING CONDITIONS: COMPREHENSIVE TESTS

Fuel flow, l/s (BPD)	0.386 (210)
Heat input, MW (million Btu/hr)	16.3 (55.5)
Feedwater flow, l/s (BPD)	6.72 (3,650)
Steam pressure, MPa (psig)	4.55 (660)
Air flows (percent)	
Diffusion	36
Premix	54
Overfire	10
FGR rate (percent)	9.5
Steamer efficiency (percent)	82.8

TABLE 3-4. STEAMER THERMAL EFFICIENCY

Heat loss efficiency (percent)	
Dry gas loss	6.8
Loss due to fuel moisture	--
Loss due to water from the combustion of fuel hydrogen	6.3
Loss due to combustibles in the flyash	0.6
Radiation loss	2.0
Unmeasured loss	1.5
Total loss	17.2
Efficiency (percent)	82.8

TABLE 3-5. FLUE GAS EMISSIONS

Pollutant	Stack[a] Range	Stack[a] Average	Furnace outlet[b] Range	Furnace outlet[b] Average
As measured:				
O_2, percent dry	2.7 to 3.3	3.0	2.4 to 2.7	2.5
CO_2, percent dry	13.1 to 13.5	13.3	14.4 to 14.5	14.4
NO_x, ppm dry	108 to 115	106	110 to 112	111
N_2O, ppm dry	12.9 to 20.5[c]	17.0	--[d]	--[d]
CO, ppm dry	45 to 135	93	68 to 75	71
TUHC, ppm dry	<1	<1	--[d]	--[d]
SO_2, ppm dry				
Continuous monitor	--[d]	--[c]	550 to 610	600
Method 8	--[e]	594	--[d]	--[d]
SO_3, ppm	--[e]	3.1	--[d]	--[d]
Method 8				
Bacharach smoke number	8	8	--[d]	--[d]

Corrected to 3% O_2	ppm	ng/J[f]	lb/million Btu[f]	ppm	ng/J[f]	lb/million Btu[f]
NO_x (as NO_2)	106	73.7	0.171	108	77.2	0.179
N_2O	17	11	0.026	--[d]	--[d]	--[d]
CO	93	39	0.091	69	29	0.069
TUHC (as CH_4)	<1	<0.2	<0.001	--[d]	--[d]	--[d]
SO_2						
Continuous monitor	--[d]	--[d]	--[d]	584	565	1.31
Method 8	594	574	1.34	--[d]	--[d]	--[d]
SO_3 (as H_2SO_4)						
Method 8	3.1	4.5	0.010	--[d]	--[d]	--[d]
Particulate	mg/dscm					
Method 5	39	14	0.033	--[d]	--[d]	--[d]
SASS	118	30	0.071	--[d]	--[d]	--[d]
Andersen	579	219	0.0489	--[d]	--[d]	--[d]

[a]Emission measurements by Acurex.
[b]Emission measurements by Getty Oil Company.
[c]Range over duplicate analysis of 6 separate gas samples.
[d]Measurement not performed at this location.
[e]Extractive sampling procedure, range not applicable.
[f]Heat input basis.
[g]Average of two trains run.

The data in Table 3-5 show relatively good agreement between the monitor measurements at the stack and furnace outlet locations. In addition, there was good agreement between the flue gas SO_2 levels measured with a continuous monitor at the furnace outlet and by the Method 8 train run at the stack.

The Method 8 results suggest that SO_3 represents about 0.5 percent of the total sulfur oxides present in the flue gas. This ratio is significantly lower than the 5 to 10 percent range typical for residual oil-fired utility and industrial boilers (Reference 3-2). The SO_2 and SO_3 levels measured by Method 8 in the flue gas would be as expected for complete conversion of all the sulfur in a 1.2 weight percent sulfur fuel oil with heating value as noted in Table 2-1. This compares favorably to the 1.06 percent sulfur content measured in the fuel.

Particulate emissions were measured at 39 mg/dscm by Method 5, 118 mg/dscm by SASS, and 57 mg/dscm as an average of two Andersen impactor trains. These are in fair agreement. The Method 5 result is the most trustworthy, since this reference method involves a multipoint (traverse) isokinetic sampling procedure.

Particle size distribution results from the two Andersen impactor trains run are shown in Figure 3-6. Results from the two runs are similar. The mean particle diameter of emitted particulate was in the 3 to 4 μm range, for runs 1 and 2, respectively.

Emissions of nitrous oxide were also measured in these tests. The level noted, at 17 ppm, is about 16 percent of the NO_x emission level. Tests of several other fossil fuel combustion sources have shown that N_2O emissions are generally in the range of 20 percent of the NO_x emission level. These

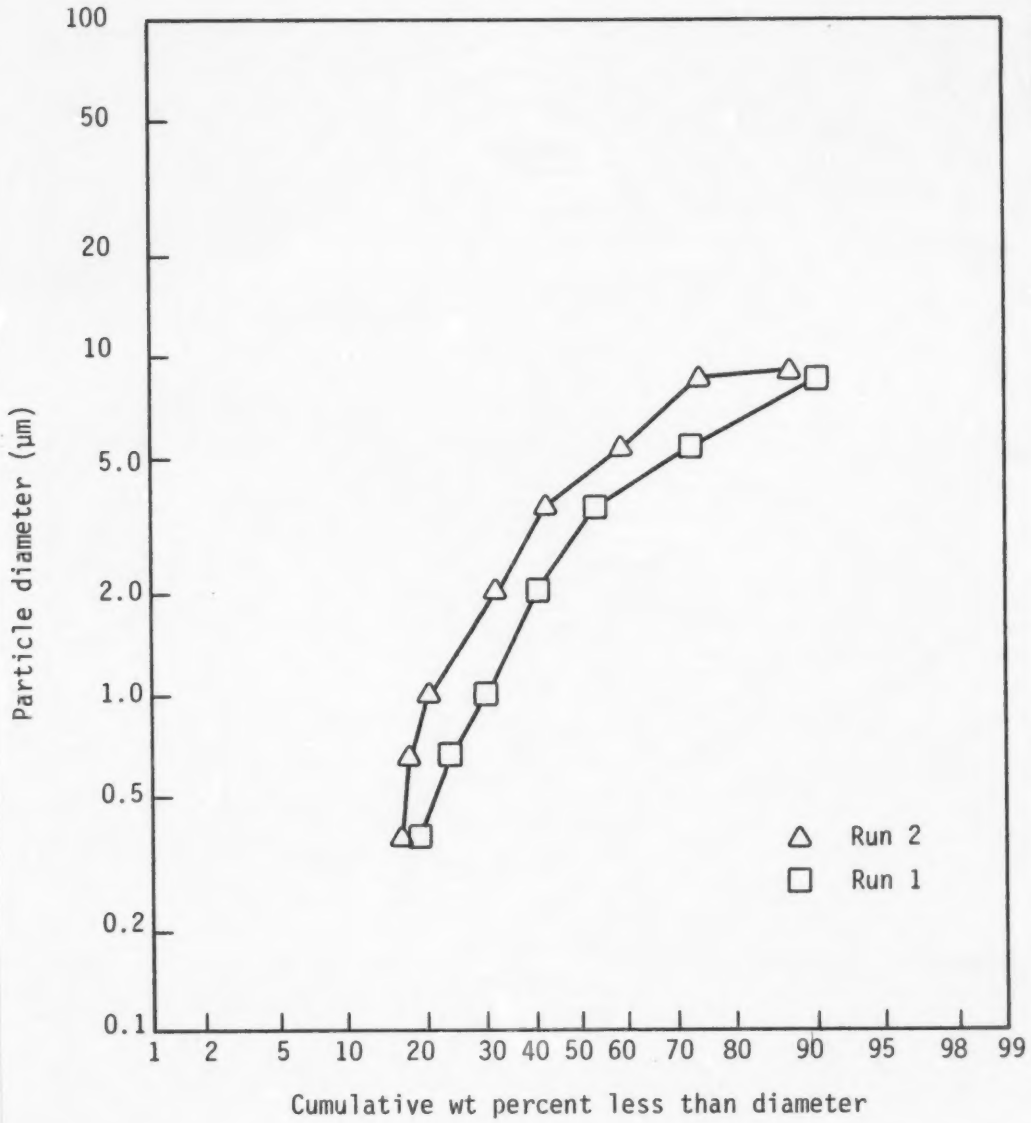


Figure 3-6. Emitted particle size distribution.

data are summarized in Figure 3-7. The point noted for this study falls on the curve corresponding to other data. The curve noted in Figure 3-7 was obtained from a least squares fit of all the data points shown in the figure, with the constraint that the curve pass through the origin. The relationship shown, $N_2O = 0.22\ NO_x$, had a corrrelation coefficient (r^2) of 0.88.

3.2.3 Organic Species Emissions

Organic analyses were performed on specified flue gas samples according to EPA Level 1 protocol (Reference 3-1) as outlined in Appendix A. Volatile organics having boiling points in the C_1 to C_6 range of less than 100°C (212°F) were determined by analysis of flue gas grab samples by onsite gas chromatography. The SASS train particulate, organic module sorbent (XAD-2), and organic module condensate (OMC) samples were extracted with methylene chloride in a Soxhlet apparatus. The extracts (XAD-2 and OMC extracts were combined) were then subjected to total chromatographable organic (TCO) and gravimetric (GRAV) analyses to determine species within the 100° to 300°C (212° to 572°F), and greater than 300°C (572°F) boiling point ranges, respectively. Infrared (IR) spectra of the GRAV residue of the extracts were also obtained.

The extracts were also analyzed via gas chromatography/mass spectrometry (GC/MS) for the semivolatile organic priority pollutant species (including many polynuclear aromatic hydrocarbons (PAH's)). Other major chromatogram peaks were identified and approximately quantitated.

Since the total organic contents (TCO and GRAV) of the extract samples were less than 15 mg, liquid chromatographic separations were not performed. However, low resolution mass spectrometry (LRMS) analysis of the particulate extract was performed.

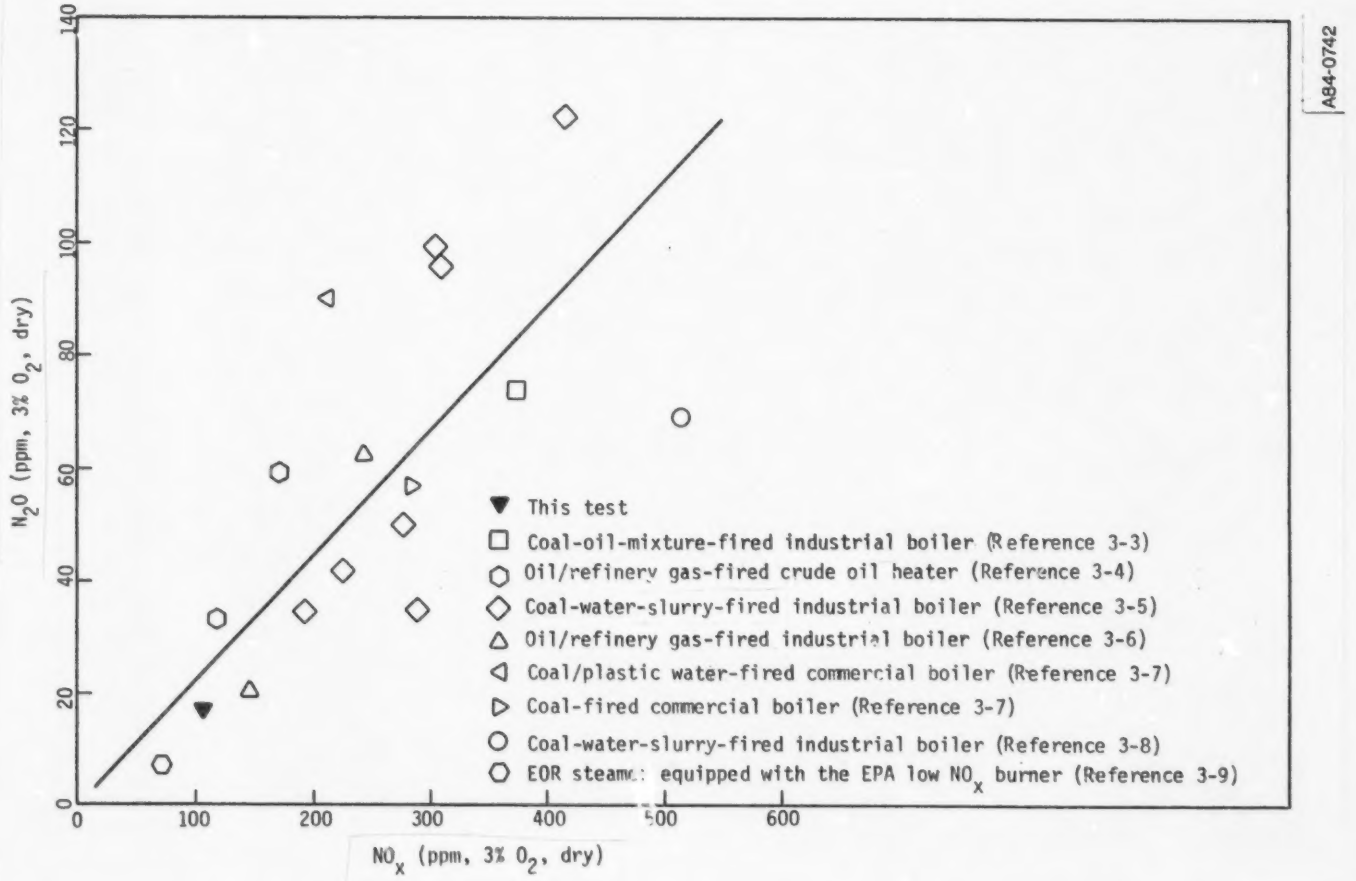


Figure 3-7. N_2O versus NO_x emissions for external combustion sources.

3.2.3.1 Total Organic Analysis

Table 3-6 summarizes measured organic emissions from the low NO_x burner-equipped steamer by organic boiling point range. The organic emissions are dominated by the volatile (C_1 to C_6) fraction, which is further composed primarily of compounds in the C_3 and C_4 boiling range. No semivolatile organics were detected. Nonvolatile organics (nominally C_{16+}) were found in the particulate, though not in the sorbent module. This confirms the high smoke emissions for the tests and suggests soot formation was occurring.

The C_1, C_3, and C_4 volatile hydrocarbon levels noted in Table 3-6 correspond to 0.3, 4.6, and 0.9 ppm, respectively, as measured. The total hydrocarbon monitor (which was unheated) read <1 ppm (see Table 3-5) for the tests. The two measurements are in fair agreement; most C_4 would not reach the total hydrocarbon monitor, and the response factor for C_3 hydrocarbon would be less than 1 ppm (as methane).

3.2.3.2 Infrared Spectra of Total Sample Extracts

The results of the IR spectrometry analysis of total sample extracts are summarized in Table 3-7. The SASS particulate spectrum suggest only the presence of aliphatic hydrocarbons in the organic fraction. The XAD-2 extract spectrum is consistent with the presence of oxygenated species such as carboxylic acids and alcohols. An interpretable spectrum for this sample was obtained despite its low organic content as noted in Table 3-6.

3.2.3.3 Low Resolution Mass Spectrometry Analysis of Total Sample Extracts

The SASS particulate extract was subjected to LRMS analysis via direct insertion probe to obtain compound category composition information. The compound categories searched for with the characteristic ions used to

TABLE 3-6. TOTAL ORGANIC EMISSIONS SUMMARY

Organic category	mg/dscm	ng/J
Volatile organics analyzed in the field by gas chromatography		
C_1	0.2	0.07
C_2	0	0
C_3	8.4	3.0
C_4	2.2	0.80
C_5	0	0
C_6	0	0
Total C_1-C_6	10.8	3.9
Semivolatile organics analyzed by TCO		
Filter	--	--
XAD-2	<0.004	<0.001
Total C_7-C_{16}	<0.004	<0.001
Nonvolatile organics analyzed by gravimetry		
Filter	0.3	0.11
XAD-2	<0.1	<0.04
Total C_{16+}	0.3	1.1
Total organics	11.1	4.0

TABLE 3-7. SUMMARY OF INFRARED SPECTRA OF TOTAL SAMPLE EXTRACTS

Sample	Wave number (cm^{-1})	Intensity	Possible assignment	Possible compound categories present
Particulate extract	2980-2910	Strong	C-H stretch	Aliphatic hydrocarbons
XAD-2	3500-3020	Strong	O-H stretch	Oxygenated hydrocarbons such as carboxylic acids or alcohols
	1660	Strong	C=O stretch	
	1270-1130	Strong	C-O stretch	

identify them are listed in Table 3-8. Table 3-9 notes compound categories found and their relative abundance (intensity). As noted, aliphatic hydrocarbons was the major organic category present in the sample. Minor categories present were ketones and heterocyclic nitrogen compounds. Specific compounds detected suggested that the ketones were chiefly fluoren-9-one, and the nitrogen heterocyclics were chiefly ethyl carbazole. The LRMS results suggest that fluoren-9-one and ethyl carbazole were present at levels in the 250 µg/g of particulate range. Confirmation of this by GC/MS is discussed in Section 3.2.3.4.

3.2.3.4 Gas Chromatography/Mass Spectrometry of Total Sample Extracts

Capillary column GC/MS analyses for the semivolatile organic priority pollutant species, a category which includes several polynuclear aromatic hydrocarbons (PAH's), were performed on the SASS particulate and XAD-2 extracts. The compounds sought in the analyses and their respective detection limits are listed in Table 3-10. In addition, major peaks in the chromatogram, other than these compounds, were identified and quantitated. Results of the analyses are summarized in Table 3-11.

Of the PAH's, only naphthalene, phenanthrene, and pyrene were found, and, except for the naphthalene, which was present at the highest concentration, these were found only in the particulate. The other species detected were generally oxygenated aromatics and fused aromatics. Benzoic acid was present at relatively high levels, followed by fluoren-9-one and ethyl carbazole. The levels of the fluorenone and ethyl carbazole, at 180 and 110 µg/g particulate respectively, confirm the qualitative results of the LRMS analyses discussed in Section 3.2.3.3.

TABLE 3-8. COMPOUND CLASSES AND FRAGMENT IONS SEARCHED FOR BY DIRECT INSERTION PROBE LRMS

Compound class	Fragment ions (m/e^-)
Polynuclear aromatic hydrocarbons	178,202,216,228,252,276
Aliphatic hydrocarbons	57,71
Halogenated aliphatics	49,63,79,81,93,95,107,109
Aromatic hydrocarbons	50,51,77,78,79,91
Ethers	45,59,73
Alcohols	45,59,61,73,75
Phenols	51,77,94
Nitriles	54,68,82
Phthalate esters	149,167
Amines	44,58
Ketones	51,71
N-heterocyclics	117,129,167,179
Mercaptans, sulfides	47,61,75
Benzothiophenes	57,58,59,69,70,85,97,111,125
Carboxylic acids	60,73,149
Amides	58,72,86,100

TABLE 3-9. SASS PARTICULATE EXTRACT LRMS RESULTS[a]

Intensity[b]	Category	MW range
Major categories		
100	Aliphatic hydrocarbons	150 to 250
10	Hetercyclic nitrogen compounds	150 to 200
10	Ketones	150 to 200
1	Polynuclear aromatic hydrocarbons	150 to 250
Specific compounds		
10	Fluoren-9-one	180
10	Ethyl carbazole	195

[a]Total organic content of this sample is 3.0 mg/g particulate, GRAV compounds.
[b]100: major component; 10: minor component; 1: trace component.

TABLE 3-10. COMPOUNDS SOUGHT IN THE GC/MS ANALYSIS AND THEIR DETECTION LIMITS (ng/μl INJECTED)

Acid compounds			
2,4,6-trichlorophenol	5	2-nitrophenol	5
p-chloro-m-cresol	5	4-nitrophenol	20
2-chlorophenol	5	2,4-dinitrophenol	20
2,4-dichlorophenol	5	4,6-dinitro-o-cresol	20
2,4-dimethylphenol	5	pentachlorophenol	5
		phenol	1
Base neutral compounds			
1,2,4-trichlorobenzene	1	benzo(c)phenathrene	40
1,2-dichlorobenzene	1	bis(2-chloroethoxy)methane	1
1,2-diphenylhydrazine (as azobenzene)	1	bis(2-chloroethyl)ether	1
		bis(2-chloroisopropyl)ether	1
1,3-dichlorobenzene	1	bis(2-ethylhexyl)phthalate	1
1,4-dichlorobenzene	1	butyl benzyl phthalate	1
2,4-dinitrotoluene	1	chrysene	1
2,6-dinitrotoluene	1	di-n-butyl phthalate	1
2-chloronaphthalene	1	di-n-octyl phthalate	1
3,3'-dichlorobenzidine	5	dibenzo(a,h)anthracene	5
3-methyl cholanthrene	40	dibenzo(c,g)carbazole	40
4-bromophenyl phenyl ether	1	diethyl phthalate	1
4-chlorophenyl phenyl ether	1	dimethyl phthalate	1
7,12-dimethyl benz(a)anthracene	40	fluoranthene	1
N-nitrosodi-n-propylamine	5	fluorene	1
N-nitrosodimethylamine	NA	hexachlorobenzene	1
N-nitrosodiphenylamine	1	hexachlorobutadiene	1
acenaphthene	1	hexachlorocyclopentadiene	1
acenaphythylene	1	hexachloroethane	1
anthracene	1	indeno(1,2,3-cd)pyrene	5
benzo(ghi)perylene	5	isophorone	1
benzidine	20	naphthalene	1
benzo(b)fluoranthene	1	nitrobenzene	1
benzo(k)fluoranthene	1	perylene	40
benzo(a)anthracene	1	phenanthrene	1
benzo(a)pyrene	1	pyrene	1

TABLE 3-11. COMPOUNDS DETECTED IN THE GC/MS ANALYSES

Species	Filter particulate[a] (µg/g)	(µg/dscm)	XAD-2 extract[a,b] (µg/dscm)	Total flue gas[c] (µg/dscm)
Semivolatile organic priority pollutants				
Naphthalene	1.6	0.19	1.2	1.4
Phenanthrene	2.6	0.30	<0.04	0.30
Phenol	1.9	0.22	<0.04	0.22
Pyrene	0.97	0.11	<0.04	0.11
Other compounds identified				
Benzofurandione	--	--	0.44	0.44
Benzoic acid	--	--	34	34
Benzothiazole	28	3.3	--	3.3
Dichlorodibenzosulfone	--	--	0.52	0.52
Ethyl benzoate	--	--	0.40	0.40
Ethyl carbazole	110	13	--	13
Fluoren-9-one	180	20	--	20
Terphenyl	45	5.2	--	5.2

[a]27.0 dscm sampled, 3.11g particulate on filter.
[b]Average of duplicate injections.
[c]Sum of average of duplicate XAD-2 result plus filter result.

REFERENCES FOR SECTION 3

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3-2. Waterland, L. R., et.al., "Environmental Assessment of Stationary Source NO_x Control Technologies --Final Report," EPA-600/7-82-034, NTIS PB82-249350, May 1982.

3-3. DeRosier, R., "Environmental Assessment of a Watertube Boiler Firing Coal/Oil Mixture," Acurex Report TR-81-87/EE, March 1984.

3-4. DeRosier, R., "Environmental Assessment of a Crude-Oil Heater Using Staged Air Lances for NO_x Reduction," Acurex Report TR-82-94/EE, November 1983.

3-5. DeRosier, R., and L. R. Waterland, "Environmental Assessment of a Watertube Boiler Firing a Coal-Water-Slurry," Acurex Report TR-84-156/EE, February 1985.

3-6. Castaldini, C., et.al., "Environmental Assessment of NH_3 Injection for an Industrial Package Boiler," Acurex Draft Report TR-83-139/EE, November 1983.

3-7. Waterland, L. R., et.al., "Environmental Assessment of a Commercial Boiler Firing a Coal/Plastic Waste Mixture," Acurex Draft Report TR-85-__/EE, February 1985.

3-8. VanBuren, D., and L. R. Waterland, "Environmental Assessment of a Coal-Water-Slurry-Fired Industrial Boiler," Acurex Draft Report TR-84-155/EE, March 1985.

3-9. Castaldini, C., et al., "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with the EPA Low NO_x Burner," Acurex Draft Report TR-85-174/EE, January 1985.

SECTION 4

QUALITY ASSURANCE ACTIVITIES

Specific quality assurance (QA) activities performed to determine the accuracy and precision of the laboratory analyses performed on samples collected in this test program included:

- Spiking a sample of cleaned XAD-2 resin from the lot used in this test with TCO, GRAV, and semivolatile priority pollutant compounds and analyzing the spiked resin to determine the accuracy (recovery) of the resin extraction and subsequent analyses
- Analyzing NBS flyash for mercury to determine the accuracy of the atomic absorption technique used
- Performing duplicate TCO and GC/MS injections on the SASS train XAD-2 extract to determine the precision of these measurements

The following paragraphs discuss results of these QA activities.

4.1 ACCURACY DETERMINATIONS

A sample of XAD-2 resin from the cleaned lot used for these tests was spiked with 3.0 mg bis(2-ethylhexyl)phthalate, 200 µg tetradecane, and 100 µg each of d_8-naphthalene, phenanthrene, and pyrene. Thus, this resin contained 0.3 mg TCO compounds (tetradecane and naphthalene) 3.2 mg GRAV compounds (the phthalate, phenanthrene, and pyrene) and 100 µg each of the three polynuclear aromatics for the semivolatile organic priority pollutant analysis.

Results of the analyses of this spiked resin are shown in Table 4-1. As noted, the recovery of the TCO analysis was 125 percent, of the GRAV analysis was 81 percent, and averaged 77 percent for the GC/MS analyses. If these are interpreted to be the accuracy of these measurements, all fall within the project accuracy objective (Reference 4-1) also noted in Table 4-1.

A sample of NBS 1633a flyash was analyzed by the cold vapor atomic absorption technique used for sample determinations in this project. The analysis result was 0.18 ppm Hg in the sample; the NBS certified value is 0.16 ppm. Thus, the accuracy of this measurement was within 11 percent, again within the QA objective of ±20 percent for this measurement.

4.2 PRECISION DETERMINATIONS

The XAD-2 extract samples from the SASS train for this test were analyzed in duplicate for TCO content, and for the semivolatile organic priority pollutants and other major peaks by GC/MS. The two TCO measures were 0.087 and 0.094 ng/injection, giving a relative standard deviation of 5.5 percent. This is within the precision objective of this measurement of 10 percent (Reference 4-1).

Results of the duplicate GC/MS injections are summarized in Table 4-2. The relative standard deviations for all compounds quantitated were well within the project precision objective of 50 percent for this measurement.

TABLE 4-1. XAD-2 RESIN SPIKE AND RECOVERY RESULTS

Measurement	Spiked amount (mg)	Recovered amount (mg)	Percent recovery	Implied accuracy	Accuracy objective[a]
Total chromatographable organics (TCO)	0.3	0.4	125	+25	±50
Gravimetric organics (GRAV)	3.2	2.6	81	-19	±50
Semivolatile organic priority pollutants:					
d_8-Naphthalene	0.1	0.077	77	-23	
Phenanthrene	0.1	0.077	77	-23	
Pyrene	0.1	0.077	77	-23	
Average			77	-23	-50 +100

[a]Reference 4-1.

TABLE 4-2. DUPLICATE GC/MS ANALYSIS RESULTS FOR THE XAD-2 EXTRACT

Compound	Run 1 µg/train	Run 2 µg/train	Relative standard deviation (%)
Phenol	26	37	24.7
Benzofurandione	10	14	23.6
Benzoic acid	960	900	4.6
Dichlorodibenzosulfone	13	15	10.1
Ethyl benzoate	10	12	12.9

REFERENCE FOR SECTION 4

4-1. "Quality Assurance Plan for the Combustion Modification Environmental Assessment," Acurex Corporation for EPA Contract 68-02-2160, September 10, 1982.

SECTION 5

SUMMARY

A comprehensive emissions testing program was performed on an enhanced oil recovery steam generator (EOR steamer) equipped with an MHI PM low NO_x burner, with less detailed comparison testing performed on an identical unit equipped with a conventional North American burner.

Full load NO_x emissions from the conventional burner-equipped boiler varied from 365 ppm (corrected to 3 percent O_2) with stack O_2 of 6.6 percent to 197 ppm with stack O_2 of 2.3 percent. However, smoke emission levels were unacceptably high at the lower O_2, lower NO_x levels. A practical NO_x emission limit (acceptable CO and smoke emissions) of about 300 ppm (corrected to 3 percent O_2) with flue gas O_2 of 3.7 percent could be maintained. At 75 percent load NO_x emissions were reduced to about 250 ppm with stack O_2 of 4.0 percent and acceptable CO and smoke emissions.

Full load NO_x emissions from the low-NO_x burner-equipped steamer varied from 95 to 180 ppm (corrected to 3 percent O_2) with variations in the overall excess air level (as measured by stack O_2), the distribution of combustion air among the burner's premixed flame nozzle, diffusion flame nozzle, and overfire (OFA) air ports, and the rate of flue gas recirculation (FGR) to the burner to separate premixed and diffusion flames. Again, unacceptably high CO and smoke emissions existed at the lower NO_x conditions. A NO_x emission

level of about 110 ppm (3 percent O_2) could be maintained with acceptable CO and smoke.

Comprehensive emissions testing of the low-NO_x burner-equipped boiler was performed with the burner operation at a nominal low-NO_x setting. With 54 percent of the combustion air supplied to the burner's premix flame, 36 percent to the diffusion flame, and 10 percent to the OFA ports, and with 9.5 percent FGR and 3.0 percent stack O_2, NO_x emissions were 106 ppm, CO emissions were 93 ppm, and Bacharach smoke number was 8. At this condition SO_2 and SO_3 emissions were 594 ppm and 3.1 ppm respectively, and particulate emissions were 39 mg/dscm. The mean particle size of the particulate was in the 3 to 4 μm range (two separate impactor train runs).

Total organic emissions were 11.1 mg/dscm, 97 percent of which was in the volatile (C_1 to C_6) boiling point range; the remainder was in the nonvolatile (>C_{16}) boiling point range. The nonvolatiles were condensed on flue gas particulate and consisted largely of aliphatic hydrocarbons, heterocyclic nitrogen compounds (ethyl carbazole), and ketones (fluorenone).

Of the polynuclear aromatic hydrocarbons specifically analyzed for in flue gas emissions, only naphthalene (1.4 μg/dscm), phenanthrene (0.3 μg/dscm), and pyrene (0.11 μg/dscm) were detected. Other compounds identified as comprising the flue gas organics included benzoic acid, ethyl carbazole, and fluoren-9-one with emission levels in the 13 to 34 μg/dscm range, and phenol, benzofurandione, benzothiazole, ethyl benzoate, and terphenyl with emission levels in the 0.1 to 5.2 μg/dscm range.

APPENDIX A

SAMPLING AND ANALYSIS METHODS

Emission test equipment was provided primarily by Acurex Corporation. Onsite equipment included a continuous flue gas monitoring system; the source assessment sampling system (SASS) for particulate mass, semivolatile, and nonvolatile organic emissions measurement; a combined EPA Method 5 and 8 train for measuring particulate, SO_2 and SO_3 emissions; an Andersen cascade impactor train for measuring emitted particle size distribution; gas grab sampling equipment and an onsite gas chromatograph equipped with a flame ionization detector (GC/FID) for determining flue gas C_1 to C_6 hydrocarbon emissions; and gas grab sampling equipment for laboratory determination of N_2O emissions by gas chromatography using an electron capture detector (GC/ECD). All the above flue gas emission sampling was performed at the steam generator stack.

In addition, Getty Oil Company provided flue gas monitoring of O_2, CO_2, CO, NO_x, and SO_2 at the steam generator furnace outlet location.

The following sections summarize the equipment sampling and analysis procedures used by Acurex in the evaluation of the steam generator/low NO_x burner.

A.1 CONTINUOUS MONITORING SYSTEM

Rack-mounted monitors and recorders located in a mobile emission laboratory were used for continuous measurement of NO_x, CO, total unburned

1. In situ filter, 0.7μ, 99.999 percent efficient
2. Exhaust duct
3. 316 stainless steel probe
4. Four pass conditioner-dryer, 316 stainless steel internals
5. 3/8-inch unheated Teflon tubing
6. Teflon-lined sample pump
7. 3/8-inch heated Teflon tubing
8. Rotameter
9. 1/4-inch Teflon tubing
10. Calibration gas manifold
11. Calibration gas selector valve
12. Calibration gas cylinders
13. Backpressure regulator

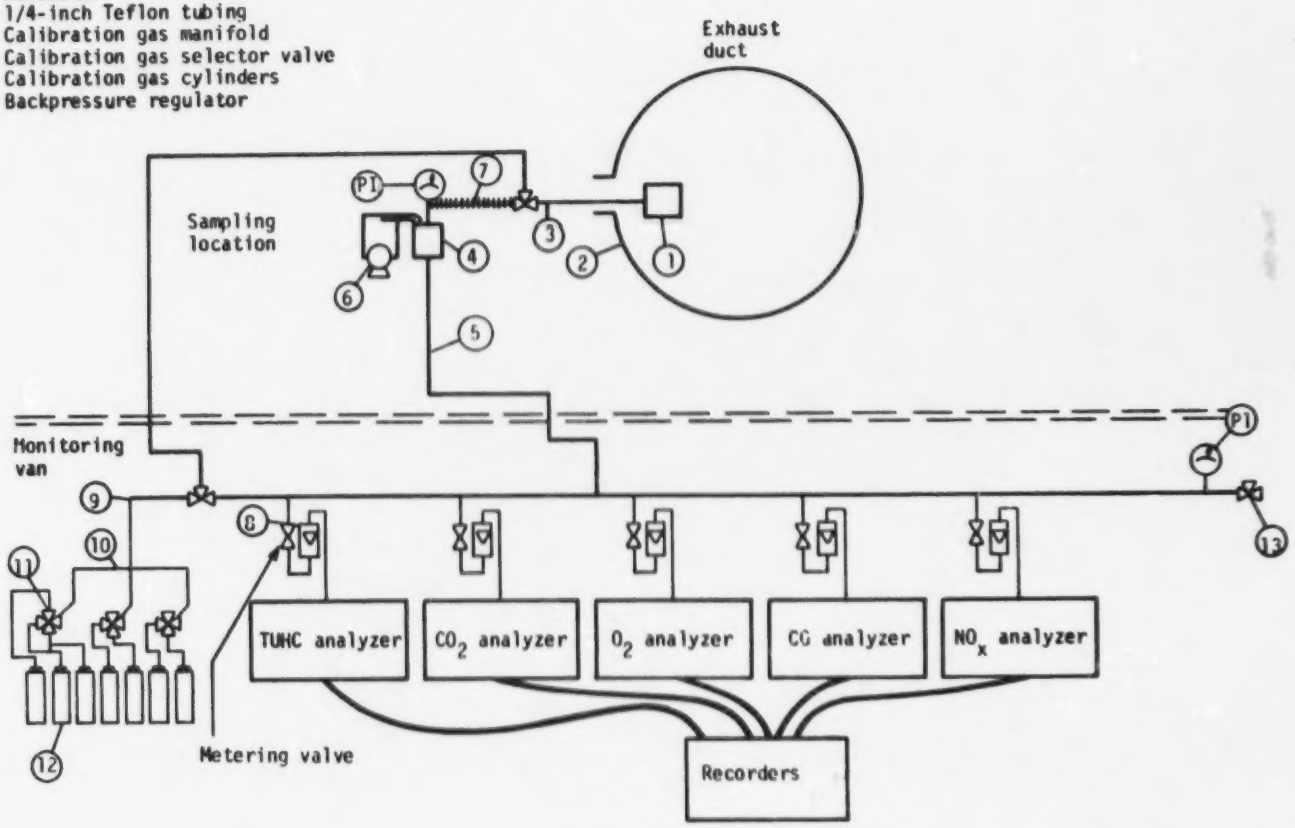

Figure A-1. Continuous monitoring system.

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hydrocarbon (TUHC), CO_2, and O_2. Figure A-1 illustrates the continuous flue gas extractive sampling system and monitors arrangement. Flue gas was drawn through an in-stack filter and a heated stainless steel probe to a gas conditioning and refrigeration system designed to remove water. An unheated line was then used to bring the conditioned gas to the monitors. Calibration gases were used to monitor and correct the drift in the instruments. The calibration gases follow the same path as the flue gas being monitored in that both are conditioned at the stack prior to analysis. Table A-1 lists the instrumentation constituting the continuous monitoring and flue gas extractive sampling system used in this test program.

A.2 PARTICULATE AND SULFUR OXIDE EMISSIONS

Particulate mass emissions were measured in accordance with EPA Reference Method 5 and SO_2 and SO_3 emissions were measured in accordance with EPA Reference Method 8. A combined Method 5/8 train employing the Acurex High Volume Stack Sampler (HVSS), illustrated schematically in Figure A-2, was used in this program. A glass-lined stainless-steel probe was used to isokinetically extract the gas sample from the stack. Particulate was removed by a heated 142 mm (5.6 in.) diameter glass fiber filter. Both the filter and the sampling probes were maintained at 120°C (250°F) as specified by Method 5.

The impinger train consisted of four glass impingers with a fritted glass filter placed between the first and second impingers as specified by Method 8. The first impinger contained 100 ml of 80 percent isopropanol (20 percent water); the second and third impingers contained 100 ml of 3 percent H_2O_2 in water; and the fourth impinger contained 200g of silica gel.

TABLE A-1. CONTINUOUS MONITORING EQUIPMENT IN THE MOBILE LABORATORY

Instrument	Principle of operation	Manufacturer	Instrument model	Range
NO NO_x	Chemiluminescence	Thermo Electron	10 AR	0-100 ppm 0-500 ppm 0-1,000 ppm 0-5,000 ppm
CO	Nondispersive infrared (NDIR)	ANARAD	500R	0-1,000 ppm
TUHC	Flame ionization detector	Beckman	400	0-10 ppm 0-100 ppm 0-1000 ppm
CO_2	Nondispersive infrared (NDIR)	ANARAD	AR500	0-20 percent
O_2	Fuel cell	Teledyne		0-5 percent 0-25 percent
Sample gas conditioner	Refrigerant dryer-condenser	Hankinson	E-4G-SS	10 scfm
Strip chart recorder	Dual pen analog	Linear	400	0-10 mV 0-100 mV 0-1V 0-10V

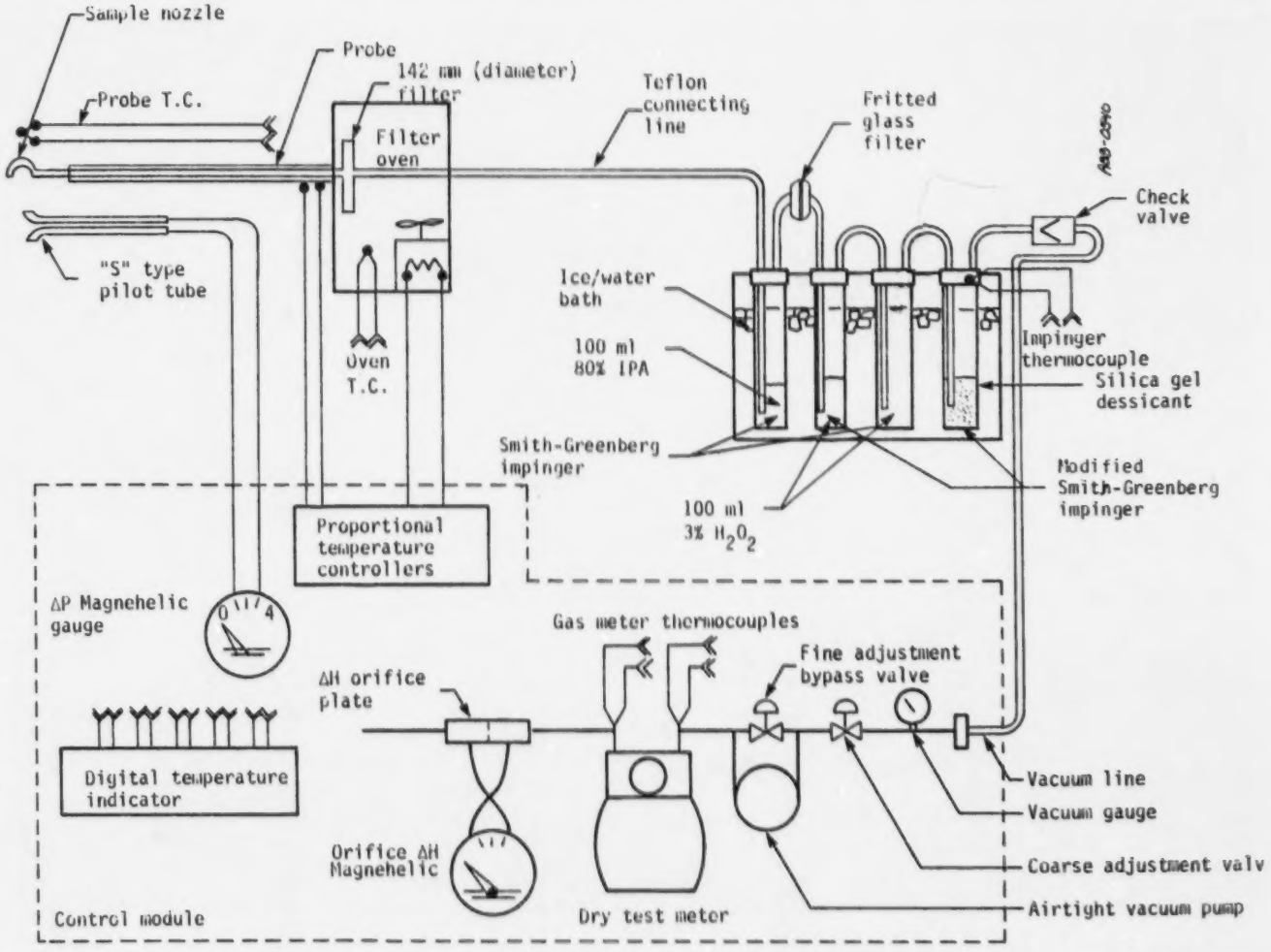

Figure A-2. Schematic of Method 5/8 sampling train.

SO_3 (H_2SO_4 mist) is collected in the first impinger and SO_2 (oxided to SO_4) in the second and third. These were determined in the laboratory by titration with 0.01N barium perchlorate using thorin indicator.

A.3 ORGANIC EMISSIONS

Emissions of organic compounds and compound categories were sampled using the source assessment sampling system (SASS). Designed for Level 1 environmental assessment (Reference A-1), the SASS collects large quantities of gas and solid samples required for subsequent analyses of inorganic and organic emissions.

The SASS, illustrated in Figure A-3, is generally similar to the system utilized for total particulate mass emission tests (a high volume Method 5 train) with the exception of:

- Particulate cyclones heated in the oven with the filter to 230°C (450°F)
- The addition of a gas cooler and organic sampling module
- The addition of necessary vacuum pumps to allow a sampling rate of 2 l/s (4 cfm)

The particulate cyclones shown were not used for these tests because of the low particulate loading in the flue gas.

Schematics outlining the standard sampling and analytical procedures using the SASS equipment are presented in Figures A-4 and A-5. The inorganic analyses of SASS train samples noted in the figures were not performed for these tests.

The SASS train particulate, XAD-2 resin, and organic module condensate (OMC) were extracted with methylene chloride in a Soxhlet apparatus. The

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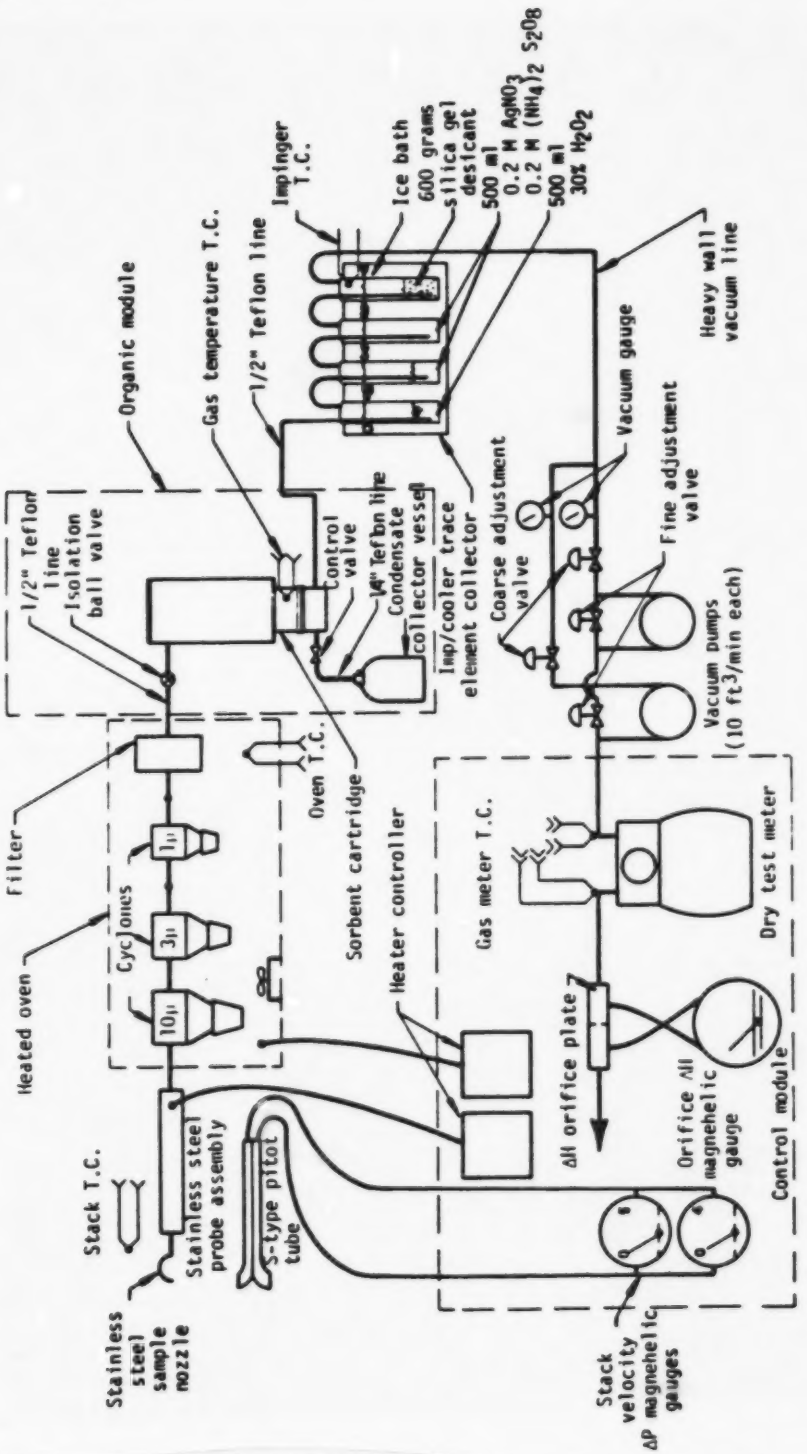

Note: T.C. = Thermocouple

Figure A-3. Source assessment sampling system schematic.

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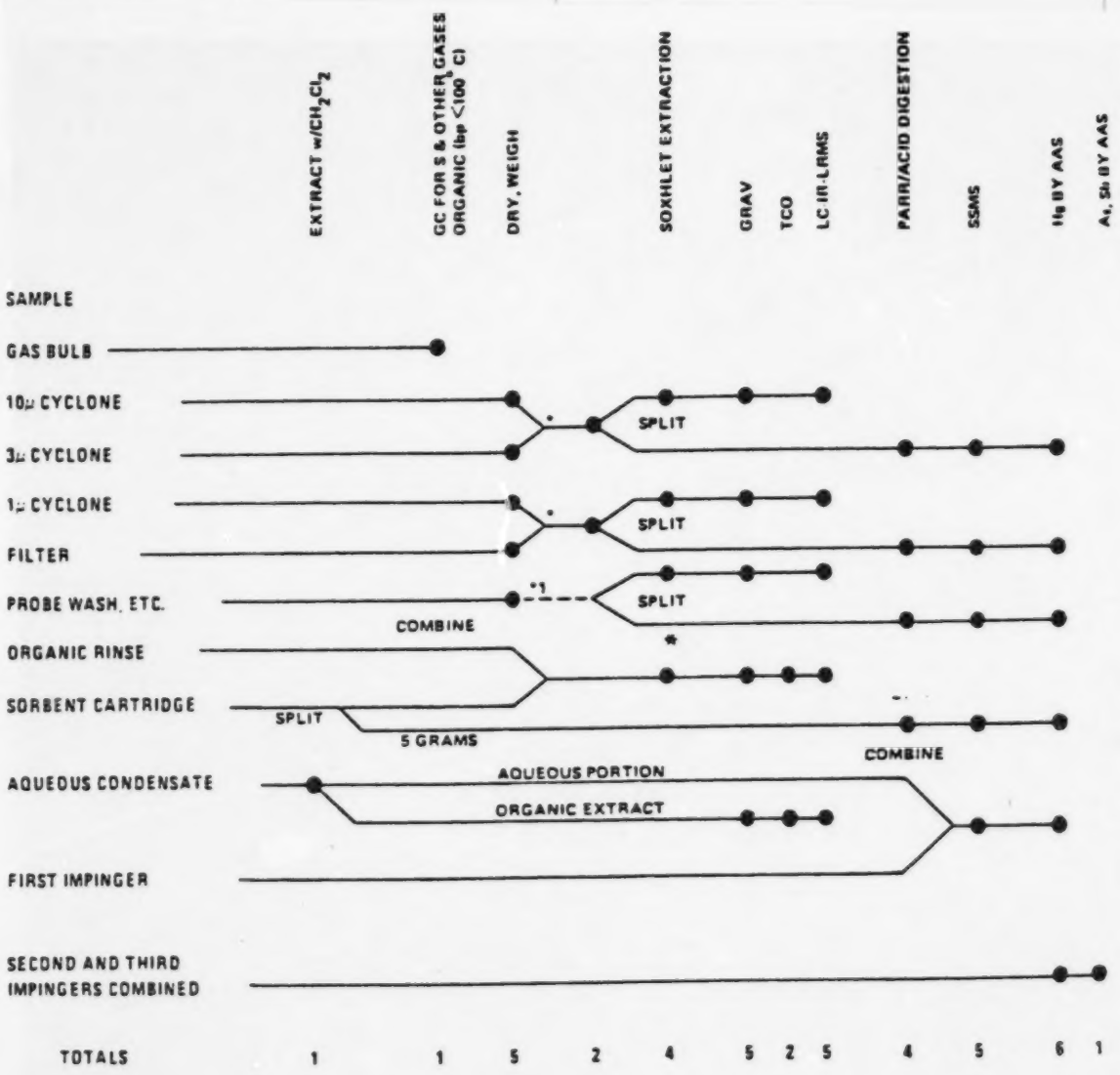

* If required, sample should be set aside for biological analysis at this point.

[1] This step is required to define the total mass of particulate catch. If the sample exceeds 10% of the total cyclone and filter sample weight proceed to analysis. If the sample is less than 10% of the catch, hold in reserve.

Figure A-4. Flue gas analysis protocol for SASS samples.

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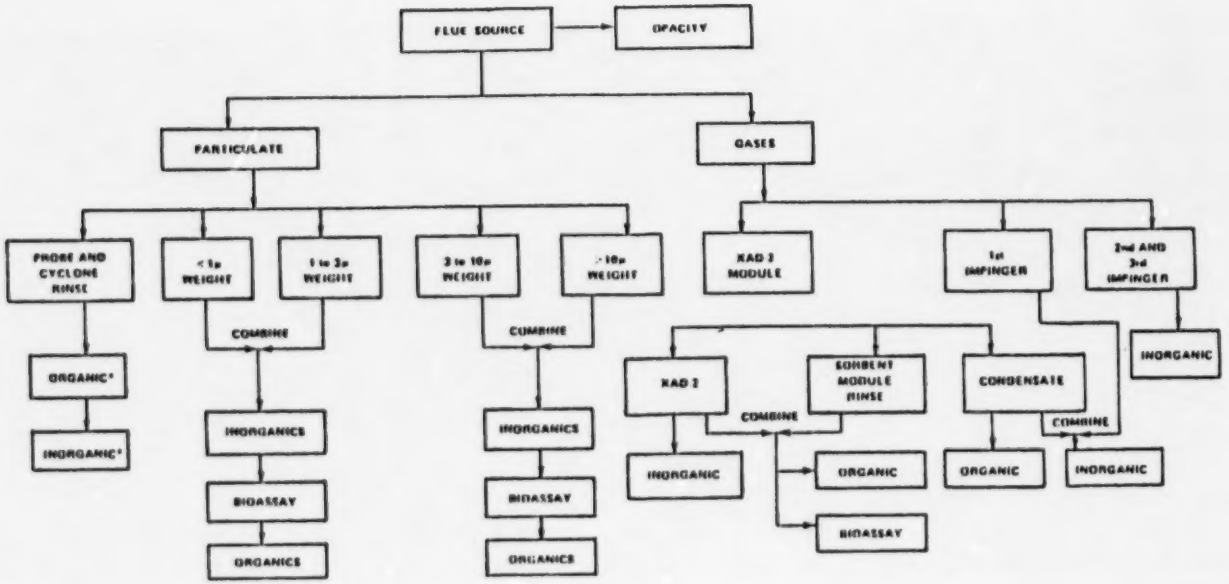

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Figure A-5. Flue gas sample analysis protocol.

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XAD-2 and OMC organic extracts were combined for analysis. The extracts were analyzed for total organic content in two boiling point ranges: 100° to 300°C (nominally C_7 to C_{16} organics) by GC/FID for total chromatographable organics (TCO) and >300°C (nominally $>C_{16}$ organics) by gravimetry (GRAV). Infrared (IR) spectra were obtained of the GRAV residue of extracts. GC/mass spectrometry (MS) in accordance with EPA Method 625 for the semivolatile organic priority pollutant species was also performed on extract samples. Extract samples containing total organic content corresponding to emissions of >0.5 mg/dscm were analyzed by low resolution mass spectrometry to identify the major compound categories present. Figure A-6 illustrates the organic analysis methodology generally followed.

A.4 PARTICLE SIZE DISTRIBUTION

An Andersen 2000 Mark III in-stack cascade impactor was used to measure particle size distribution. The impactor was preheated inside the stack for 30 minutes prior to the start of sampling. Sampling was performed isokinetically at a point of average stack gas velocity.

The Mark III impactor consists of multiple stages which collect different particle sizes. Each stage consists of orifices of a specific diameter above a collection plate containing a glass fiber substrate. The orifice sizes of each stage are different and are arranged in descending order, the largest being stage 0.

For sampling, the stack gas was drawn in through the stainless-steel nozzle into the heated preseparator and impactor. The gas flowed through a stainless-steel probe and a Teflon line into the condensor train consisting of a series of 3 Lexan impingers. The gas was then pulled through a carbon

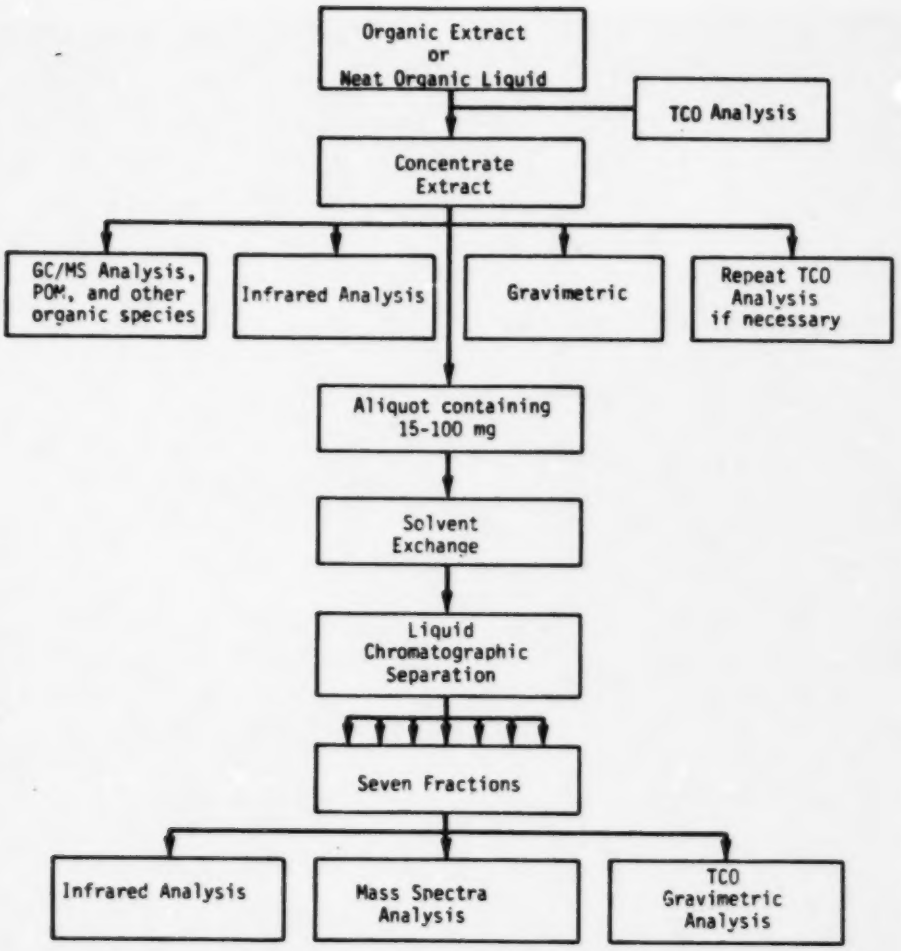

Figure A-6. Organic analysis methodology.

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vane pump, dry gas meter, and calibrated orifice. The temperature of the gas leaving the impactor and the impactor temperature were measured during each test with type K thermocouples.

After a test, the Mark III impactor was carefully disassembled and the glass fiber substrates returned to their original foil containers. Any particulate matter which adhered to the impaction plates was brushed onto the appropriate filter. The samples were desiccated for 24 hours and weighed to the nearest 0.01 mg. The nozzle and Mark III inlet cone were rinsed thoroughly with acetone into a labeled amber jar. These washings were transferred to tared aluminum pans, evaporated, then desiccated for 24 hour and weighed to the nearest 0.1 mg.

A.5 C_1 TO C_6 HYDROCARBON SAMPLING AND ANALYSIS

Samples of flue gas for C_1 to C_6 hydrocarbon analysis were collected using a grab sampling procedure employing the apparatus illustrated in Figure A-7. The equipment consisted of a heated, 0.64-cm (1/4-in.) OD pyrex-lined, stainless-steel probe fitted with a 7-μm sintered stainless-steel filter at the probe inlet. The outlet of the probe was directly attached to a diaphragm vacuum pump which was in turn attached to a 500-ml stainless-steel heated sampling cylinder. The sampling cylinder was insulated with heat tape powered by a varying voltage controller. The heating jacket kept the sample gas above the dew point to minimize sample loss due to water condensation.

Prior to sampling, the gas cylinder was purged with stack gas for 3 minutes and then sealed. The trapped flue gas was then analyzed onsite with a Varian Model 3700 gas chromatograph (GC) equipped with a flame ionization detector.

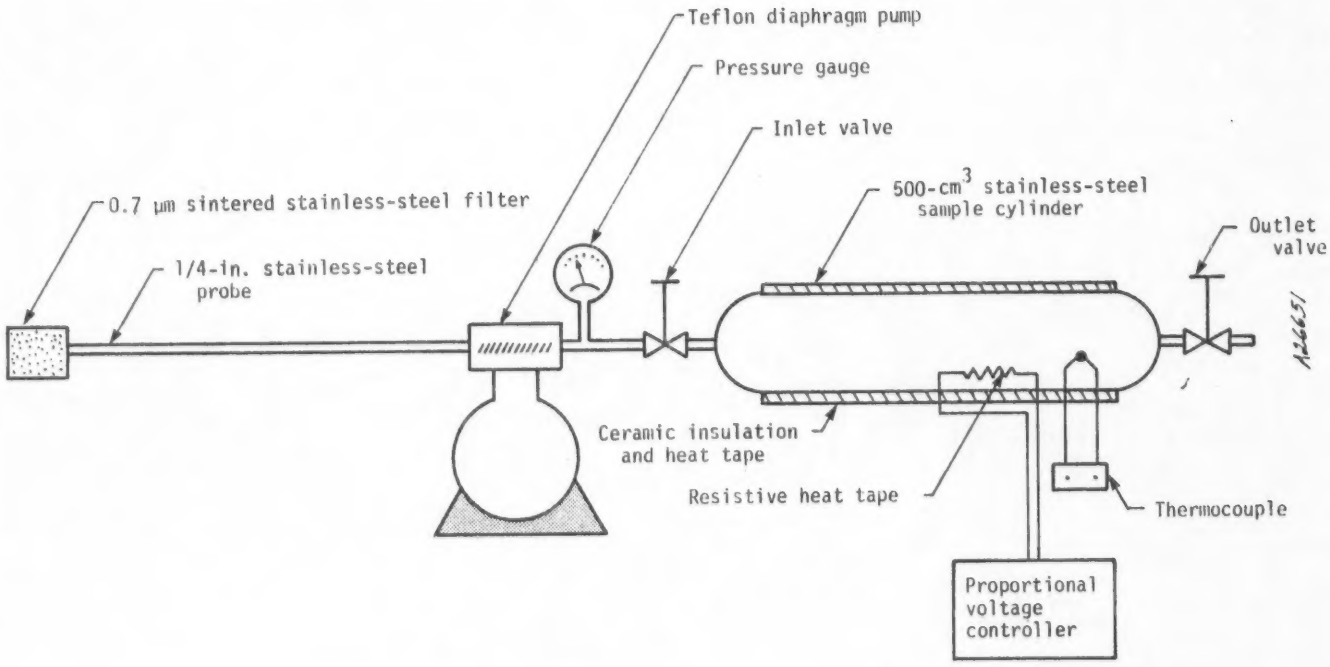

Figure A-7. C_1 to C_6 hydrocarbon sampling system.

Table A-2 lists the design specifications of the Varian GC. A 1.85m (6 ft) long, 0.32 cm (1/8 in.) diameter stainless-steel column packed with Poropak Q 60/80 mesh was used to separate the hydrocarbons into their respective components (C_1 to C_6). The GC was calibrated with repeated injections of a Scott Speciality standard gas containing C_1 to C_6 hydrocarbons (each having a concentration of 15 ppm). The chromatographic responses for the standards and the samples were recorded on a Hewlett Packard Model 3390A reporting integrator.

A.6 N_2O EMISSIONS

Stack gas grab samples were extracted into stainless-steel cylinders similar to those used for C_1 to C_6 hydrocarbon sampling (Section A.5) for laboratory analysis for N_2O. For the analysis each sample cylinder was externally heated to 120°C (250°F); then a 1-ml sample was withdrawn with a gas-tight syringe for injection into a gas chromatograph. The analytical equipment consisted of a Varian 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector and a 3.65m (12 ft) stainless-steel column packed with Poropak Super Q, 80/100 mesh. The injector temperature was kept at 80°C, the detector at 350°C, and the column temperature at 33°C. Elution time for N_2O was approximately 5 minutes, with a flowrate of 20 ml/min of nitrogen.

TABLE A-2. GAS CHROMATOGRAPH SPECIFICATIONS

Varian Model 3700 Gas Chromatograph:	
Sensitivity	1×10^{-12} A/mV at attenuation 1 and range 10^{-12} A/mV
Zero range	-10^{-11} to 10^{-9} A (reversible with internal switch)
Noise (inputs capped)	5×10^{-15} A; 0.5 μV peak to peak
Time constant	220 ms on all ranges (approximate 1 sec response to 99 percent of peak)
Gas required	Carrier gas (helium), combustion air, fuel gas (hydrogen)